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VAPOR PHASE RADIOLYSIS OF METHYLCYCLOHEXANE

BY

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Vapor Phase Radiolysis of Methylcyclohexane" submitted by WILLIAM J. HOLTSLANDER in partial fulfilment of the requirements for the degree of Doctor of Philosophy.





## A B S T R A C T

The radiolysis of methylcyclohexane (MCH) vapor has been carried out under a variety of conditions. The G-value of the main products extrapolated to zero dose are hydrogen (5.2), methylcyclohexene isomers (2.0), total dimer (0.3), methane (1.3), ethylene (1.5) and propylene (0.8). A number of other products were also measured.

The hydrogen yield was shown to consist of three parts,  $G = 2.1$  from ions,  $G = 1.5$  from hydrogen atoms, and  $G = 1.6$  of molecular hydrogen. In pure MCH approximately 50 percent of ions formed ( $G(\text{ion}) = 4.4$ ) resulted in hydrogen formation. However in the presence of  $\text{ND}_3$  or  $\text{DI}$  an additional 1.2 G-units of ions yielded hydrogen.

The methylcyclohexene isomers (MC) were formed by at least two processes, one of which was probably the disproportionation of methylcyclohexyl radicals. There is evidence that the MC yield and methylcyclohexyl radicals were partially destroyed by a secondary reaction involving positive ions.

The dimer products were formed by the combination of methylcyclohexyl radicals.

Approximately 85 percent of the methane is produced by methyl radicals abstracting a hydrogen atom from MCH.

In the radiolysis of MCH-carbon tetrachloride mixtures a free radical chain reaction produced large yields ( $G = 40$ ) of chloroform and methylcyclohexyl chloride.



It was shown that nitrous oxide does not act simply as an electron scavenger when present in the radiolysis of MCH vapor. There are large yields of nitrogen ( $G = 22$ ) and methylcyclohexene ( $G = 17$ ) produced by a chain mechanism initiated by capture of electrons by nitrous oxide.





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## INTRODUCTION

### A. BACKGROUND

The early work of S. C. Lind and coworkers in the United States and of W. Mund and associates in Belgium dominates the early history of the radiation chemistry of gases (1). These early studies were mainly carried out by exposing the gases to the  $\alpha$ -particles of radium or radon. The importance of ionization in the radiolytic decomposition of compounds was soon recognized. Lind attempted to correlate the number of molecules of material undergoing reaction with the number of ion pairs formed by the radiation. In several cases he found that the ionic yield,  $M/N$ , defined as the number of molecules formed or destroyed per ion pair, exceeded unity. A one to one correspondence between decomposition and ionization did not exist. To account for this increased decomposition, Lind proposed a cluster hypothesis in which he suggested the ion formed by the radiation attracted a number of neutral molecules around it. These neutral molecules were held close to the ion by polarization forces. Upon neutralization of the clustered ion, the heat of neutralization was distributed among all the molecules in the cluster. These excited molecules could then undergo reaction. This theory satisfactorily explained the large  $M/N$  values observed in many systems.

In addition to the formation of ions, excited molecules are also formed directly in compounds exposed to radiation. These excited



molecules can either react or dissociate into free radicals, atoms, and stable molecules. Because of the similarity of products observed in the polymerization of ethylene induced by the thermal decomposition of mercury diethyl to those found in the  $\alpha$ -particle radiolysis studies of Lind, Bardwell and Perry (2) in ethylene, Taylor and Jones (3) questioned

"... whether it is necessary in the  $\alpha$ -particle experiment to assume clustering around ions or whether one should not assume the formation of radicals as a resultant of the action of the  $\alpha$ -particle followed by a sequence of chemical processes identical with those obtained as a result of the introduction to such systems of either atomic hydrogen or free radicals."

Capron (4) observed the conversion of para- to ortho-hydrogen under alpha radiation proceeded with an ionic yield of 700-1000, and concluded the mechanism involved a H atom chain reaction. This interpretation was later substantiated by theoretical treatment of the ortho-para conversion of hydrogen by Eyring, Hirschfelder and Taylor (5). Their theory showed that in this system hydrogen atoms were produced both directly by the radiation and by ion neutralization. These hydrogen atoms then initiated a chain reaction which produced the high exchange yields. Ion clusters were shown to be unimportant in hydrogen. The theory also gave a satisfactory explanation of Lind and Livingstone's (6) data on the HBr radiolysis system (7), and later to the behavior of CO, CO<sub>2</sub>, O<sub>2</sub> and mixtures of these gases under irradiation (8). They found the experimental data on these chemical systems could be explained by the reactions of atoms and radicals produced from excited molecules.





The excited molecules were formed by the direct absorption of energy from the radiation and by neutralization of ions. Clustering of neutral molecules around a central ion was not necessary to explain the experimental results.

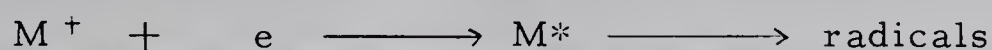
Essex and coworkers (9, 10) studied the  $\alpha$ -particle decomposition of gases in the presence of an electric field. They observed a lower ion yield of decomposition in the presence of the electric field compared to the absence of a field. The decrease was attributed to collection of ions on the electrodes which prevented gas phase recombination. The decrease of ionic yield was taken as the direct contribution of ions to the overall decomposition. In ammonia (9) they found that about one-third of the total decomposition was due to ions or ion combinations, and assumed the remainder of the decomposition was due to excited molecules. In the case of nitrous oxide (10) the fraction of the decomposition due to ions directly was less than 10 percent.

During the late 1930's and early 1940's evidence mounted against Lind's cluster hypothesis (11). In the following years it was suggested that the role of ions in radiation chemistry mechanisms was largely limited to the fragmentation of parent ions, and to the formation of excited molecules and radicals through the neutralization process (12, 13). The reactions of radicals and atoms were emphasized in the mechanisms postulated for product formation (14, 15).

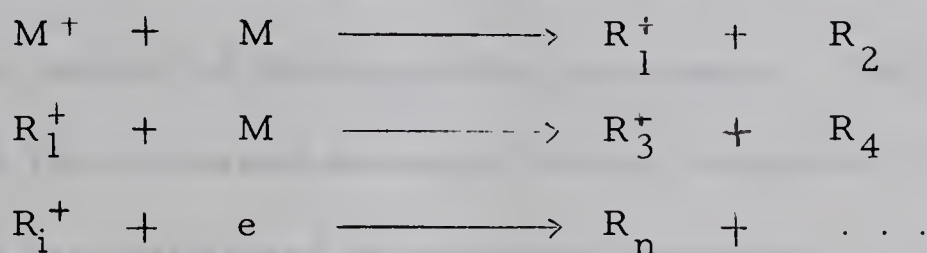
The importance of ionic reactions in radiation chemistry



mechanisms was revived by Stevenson (16) in 1957. This revival was based on the observation of fast ion-molecule reactions which occurred at every collision in a mass spectrometer (17). Stevenson estimated that at atmospheric pressure and a dose rate of approximately  $10^{20}$  ev/hr gm of air, the lifetime of an ion with respect to neutralization was greater than  $10^{-3}$  seconds and so would undergo more than  $10^8$  collision before neutralization. He suggested the radiation chemistry mechanisms could no longer be written



but must be modified:



In recent high pressure mass spectrometry studies (18) where ion source pressures of 200 Torr have been attained, polymer ions have been observed. Polymer ions of the type  $(C_2H_4)_n^+$  where  $n$  reaches 8 are found in the high pressure mass spectrum of ethylene.

During the past 60 or so years, there have been at different periods of time trends to emphasize one or another type of process to explain the effect of radiation in chemical systems. The important advance has been the realization that the overall decomposition cannot







be explained in terms of one type of process. The fact that ion decompositions, ion-molecule reactions, neutral excited molecule decompositions, and free radical reactions all must be employed to some degree is now realized. One of the important problems in modern gas phase radiolysis is to determine the relative contributions of these various processes to the overall mechanism.

As a starting point in the study of radiation induced decompositions, the determination of the initial decomposition pattern of the compound is important. The initial decomposition pattern consists of the identity and amounts of all products initially formed from the parent compound under irradiation. This pattern changes as the total amount of decomposition increases. The change of product yields with the increased amount of energy absorbed, (i.e. increased dose), has been attributed to secondary reactions. The concentrations of radiolysis products build up with increasing dose, and <sup>they</sup> start to undergo reactions with reactive intermediates in the system. This results in the formation of products not originally present in the initial decomposition, and in changes of the original product yield. This effect of secondary reactions was pointed out by Back (19) in a dose study with gaseous alkanes. Back stated that at a total decomposition as low as 0.1%, the build up of radiolysis products that could take part in secondary reactions, would be sufficient to completely obscure the initial conditions. Indirect evidence for secondary reactions comes from the poor material balance



observed in gaseous alkane radiolysis. That is, there is a larger yield of products that are hydrogen rich than there is of products that are hydrogen deficient compared to the material being irradiated.

The poor material balance has been attributed to non-detection of high molecular weight polymer products formed by secondary reactions.

Two approaches can be taken to overcome the effect of secondary reactions. The first is to work at a low overall decomposition or conversion. This will keep the concentrations of products sufficiently low so that secondary reactions will not be important. This method is limited because of analytical problems associated with measurement of the low concentration of products present. A dose of  $10^{18} - 10^{19}$  ev/g, representing approximately 0.05% decomposition, is the minimum necessary for a complete product analysis on the present analytical equipment.

The second method to counteract at least some secondary reactions, has been to add a small concentration of another compound which interferes with the secondary reaction and yet leaves the initial product yield intact. An example of this technique is the addition of nitric oxide to the radiolysis of methane (20). The ethylene yield increases in the presence of nitric oxide because the nitric oxide removes radicals that were reacting with the ethylene in the pure system. The problem with this technique is to find additive compounds that inhibit secondary reactions, but do not affect the primary processes occurring





during radiolysis. In the above example, while the initial yield of ethylene is preserved by nitric oxide addition, the yields of products that are formed by radicals are diminished.

## B. GAS PHASE DOSIMETRY

The subject of dosimetry involves measurement of the energy absorbed by the system under study. The yields of products produced in radiolytic decomposition are expressed in terms of the energy absorbed by the compound. Two common quantities are employed for reporting these yields. The ion pair yield,  $M/N$ , is the number of molecules formed or destroyed per ion pair produced in the system by the radiation. The G-value is the number of molecules formed or destroyed per 100 electron volts (ev) of energy absorbed by the sample. The energy absorbed by the sample must be known to calculate either of these quantities. These two methods of expressing yields are interconvertible if the average energy required to form an ion pair ( $W$ ) is known for the compound under study.

$$G = \frac{M}{N} \times \frac{100}{W}$$

Chemical dosimeters are commonly employed in the determination of the dose rate received by a sample. A chemical dosimeter is a compound or mixture of compounds that has a known behavior under irradiation. This known behavior may be the formation of a product with an established yield. In this method, the chemical dosimeter is



irradiated under the same conditions as the system being studied.

From the amount of the product formed and the length of time of the irradiation the dose rate delivered to the dosimeter is calculated. The dose rate received by the dosimeter is then used to calculate the dose rate received by the compound under investigation. This is done by multiplying the dosimeter dose rate by the ratio of the electron densities of the two compounds (21). In gases, the ratio of the stopping powers of the two compounds is sometimes used in place of the electron density ratio (22). The stopping powers are calculated from Bethe's equation (23).

The most commonly used chemical dosimeter at the present time is an acidic solution of ferrous sulfate, (the Fricke dosimeter). The amount of ferric ion ( $G(\text{Fe}^{++}) = 15.6$  for  $\gamma$  rays) produced per unit time is measured, and the dose rate calculated in units, such as ev per hour, per ml. This dosimeter works very well for the liquid phase where the density of the liquid being irradiated, and of the glass of the cell containing the liquid, are similar. The range of electrons produced in the Compton process (24) for  $^{60}\text{Co}$   $\gamma$ -radiation (average energy 0.6 Mev), is approximately 0.3 cm in liquid alkanes. Since the irradiation vessels used for liquids are approximately 1-2 cm in diameter, these Compton electrons are absorbed in the liquid sample. In the gas phase however, the opposite situation occurs. Because the density of a gas near atmospheric pressure is two to three orders of magnitude less than the glass wall, practically all the energy absorption from the  $\gamma$ -beam





occurs in the glass wall. The range of the 0.6 Mev electrons in air at atmospheric pressure is approximately 200 cm, which is large compared to gas phase irradiation vessels, normally about 10 cm or less in diameter. The compton electrons produced in the glass wall pass through the gas contained in the vessel with only a small fractional loss in energy (13). Back (13) estimated that the direct absorption of  $\gamma$ -rays in the gas could account for only approximately 1% of the observed decomposition in the radiolysis of 570 ml of propane at 800 Torr.

Because of the difference of energy deposition in liquids and gases, it is difficult to adapt liquid phase dosimeters to gas phase studies. Since the absorption of  $^{60}\text{Co}$   $\gamma$ -radiation in a material is proportional to the electron density of the material, there have been attempts to use the Fricke dosimeter for gas phase systems by multiplying the dose rate measured in the Fricke solution by the electron density ratio between the Fricke solution and the gas (25). The magnitude of this correction is large, and for this reason leaves the accuracy of the dosimetry in doubt.

A number of gas phase chemical dosimeters have been used for radiolysis studies of alkane vapors. The radiation induced polymerization of acetylene to benzene and cuprene with a consumption of acetylene of  $G(-\text{C}_2\text{H}_2) = 71.9$  (26), has been used (27). The nitrogen yield from nitrous oxide has also been suggested as a gas phase dosimeter (28).



However, there is a wide variation of nitrogen yields reported (25, 28, 29, 30) which makes the use of nitrous oxide undesirable. The hydrogen yield from ethylene is quite widely used for dosimetry. Yields of  $G(H_2)$  from 1.2 to 1.3 have been reported (31, 32, 33). Even this variation results in an uncertainty of 8% in the dose rate.

The most direct method for dosimetry in gas phase systems is the saturation current method (22, 31). A special cell is used which contains the gas between two electrodes. When a voltage is applied across the electrodes during irradiation of the cell, the radiation induced current gradually builds up with increasing voltage. The current rises to a plateau value which is independent of the applied voltage. This plateau current, called the saturation current, represents the collection on the electrodes of all the ions produced by irradiation of the gas in the cell. The saturation current is measured as a function of pressure (moles of gas) in the cell. From these measurements, a J-value, defined as the number of amps per mole of gas, is calculated. The dose rate is given by the following equation:

$$\text{Dose Rate (ion pairs/mole sec)} = J/e$$

where  $e$  = electronic charge =  $1.602 \times 10^{-19}$  coulomb. For reporting ion pair yields this dose rate is sufficient. To convert the dose rate into terms of energy for calculation of G-values, it is necessary to multiply the above dose rate by the W value for the gas irradiated.

Air is commonly used for dosimetric purposes in the saturation





current method (34). The W-value for air is reasonably well established at 33.8 ev (35, 36). The dose rate in air is converted to the dose rate in the compound of interest by multiplying by the ratio of stopping powers as mentioned previously. (Detailed calculations of these stopping power ratios are given in Appendix ).

### C. DETERMINATION OF W-VALUES

The energy required for ionization of gases by radiation is measured by W, the average energy required to form an ion pair. The recent emphasis on the importance of ionic mechanisms in radiation chemistry has sparked much interest in W-values, since the yield of ions produced by irradiation of gas can be calculated from the W-value.

$$G(\text{ion}) = \frac{100}{W(\text{ev})}$$

The common method employed to measure W-values of compounds of interest in radiation chemistry is a comparative method, using as a standard some gas for which the W-value is well known (36). Reference gases used for W-measurements include helium, neon, argon and air. The technique involves the measurement of saturation currents and J-values in the reference and unknown gases under the same radiolytic conditions. The W-value of the unknown gas,  $W_X$ , is calculated from the following equation:

$$W_X = W_{\text{STD}} \times \frac{J_{\text{STD}}}{J_X} \times \rho_{\text{STD}}^X$$

where  $\rho_{\text{STD}}^X$  is the ratio of stopping powers of the unknown and standard



gases.

Absolute W-values can be measured by use of a Wilson cloud chamber. The energy loss per unit path length is obtained from the change in curvature of the electron path in a known magnetic field, and the number of ions per unit path length are counted. W is the ratio of these two quantities. A second absolute method is to absorb completely a radiation of known energy in an ion chamber and collect at electrodes all of the ions produced. The value of W is then calculated from the "saturation current", and the amount of radiation energy absorbed.

While the experimental measurement of W-values is reasonably straightforward in principle, there are some phenomena that can interfere with the collection of ions. These difficulties have been reviewed by Platzman (37, 38) and are only outlined briefly here.

Partial recombination of the positive and negative ions before they are collected on the electrodes will result in an apparent increase in W. This phenomenon is restricted to electronegative gases which are capable of forming negative ions. With other gases such as organic vapors, where negative ions are unlikely, and the collection of electrons is efficient, there is little problem of ion recombination. Recombination is more important for densely ionizing radiation such as  $\alpha$ -particles, than it is for electron irradiation.

The number of ions produced by the radiation can be enhanced by a number of secondary processes.





1) An impurity molecule (X) may be ionized by a metastable electronically excited molecule (M\*) of the main gas.



This process was identified by Jesse and Sadauskis (39, 40) and is now referred to as the Jesse effect. Ionization of the impurity molecule X may occur if the main gas has a metastable excited state of higher energy than the ionization potential of X. Under these conditions the energy transfer will occur on every collision. A further requirement is that M\* be sufficiently long lived to undergo a collision with the impurity molecule. For He, Ne, Ar the Jesse effect occurs at impurity concentrations of  $\sim 0.1 \text{ mole\%}$  in the gases at one atmosphere pressure.

A modification of process 1) may occur if the impurity X is a polyatomic molecule rather than an atom, and the energy transferred by M\* is not greatly in excess of the ionization potential of X. The energy transferred may cause dissociation of X or be converted into heat rather than cause ionization.

Because of the lack of metastable excited states in saturated hydrocarbons (38) the existence of the Jesse effect is negligible in these compounds. Thus the W-values for these organic vapors should not be altered by the presence of trace impurities.

2) An excited molecule (M\*) may be converted into a dimeric ion.



This reaction occurs with excited atoms of the alkali metal vapors and



rare gases, but its occurrence in molecular gases remains unknown. Platzman (38) suggests it may be important for small molecules, but for large molecules rapid internal dissipation of the excitation energy is more likely to occur.

3) An impurity molecule may be ionized by collision with an electron.



The above reaction occurs with electrons of energy lower than the lowest electronic excitation potential of the main gas. If an impurity X with a sufficiently low ionization potential is present, then ionization by these sub-electronic excitation electrons could occur. Little is known about this process, particularly in molecular gases.

The magnitude of the W-value is always greater than the ionization potential for the same compound. For the rare gases, W/I is essentially constant at 1.7; for molecular gases, including organic and inorganic compounds, W/I lies in the range from 2.1 to 2.6 (37). This means that approximately equal amounts of energy are deposited in the forms of ionization and excitation.

Some regularities in the magnitudes of W-values of organic gases have been observed. Meisels (35) pointed out that W values decrease with increasing chain length for both the alkane and alkene series. The W-value for an olefin is higher than that for the corresponding saturated compound.

In molecular gases the W-values measured with  $\alpha$ -particle





radiation are found to be higher than those measured using  $\gamma$ -rays (38) ( $W_{\alpha} / W_{\beta} = 1.05-1.07$ ). Hydrogen is the exception and falls in with the rare gases where  $W_{\alpha} / W_{\beta}$  is unity. This experimental observation is not yet understood.

From this summary it is seen that saturation current measurements for organic vapors are not affected by the majority of the phenomena causing errors in similar measurements with monatomic gases. Thus, the W-values for organic gases by the simple comparative technique should be reasonably accurate.

#### D. GAS PHASE RADIOLYSIS OF ALKANES

##### 1. Information from other fields

Since the absorption of radiation by organic vapors results in the formation of excited molecules, free radicals and ions, it is natural that information obtained from photochemical and mass spectrometric studies be used to assist in the formulation of radiolysis mechanisms. Information concerning reactions of free radicals and excited molecules is obtained from conventional photochemistry, while data on ionic reactions come from photoionization by light in the vacuum ultra-violet region and from mass spectrometry.

Radiolysis studies are often carried out in conjunction with photolysis of the same compound under similar conditions. The products from photolysis are formed only by free radical reactions or by decomposition of neutral excited molecules. If similar products and





product distributions are observed in the radiolysis, then reactions analogous to those in the photolysis can be postulated. This technique was used by Ausloos (41) to show that decomposition of neutral excited molecules do play a part in gas phase radiolysis.

Photolysis with vacuum ultra-violet light of energy high enough to produce ionization has been employed to study the reactions of specific ions. The wavelength of the incident light can be chosen such that the parent ion of a compound will be formed, but fragment ions will not. For example, in the photoionization of propylene (42) (ionization potential 9.73 ev), with light of 10.0 ev (Kr 1236 Å line), only  $\text{C}_3\text{H}_6^+$  ions were formed. The fragment ions all have appearance potentials above 10 ev. The ionic reactions with added alkanes, (of ionization potential greater than 10 ev) that were studied in this system, could only have involved the  $\text{C}_3\text{H}_6^+$  ion.

The mass spectrum of a compound represents the decomposition into ions under electron impact. Since the importance of ion-molecule reactions has been established (3), there has been a trend to relate the decomposition of a compound in the mass spectrometer to the products observed in gas phase radiolysis. Futrell (43, 44) calculated the yields of products expected from the radiolysis of n-hexane and n-pentane vapor, on the basis of their mass spectra. The assumptions made in these calculations were:

- 1) The parent molecules are ionized by fast electrons and the parent



molecule ions decompose into fragment ions with the same mass distribution as shown from the mass spectrum of the compound.

2) These fragment ions react at every collision with a neutral molecule, primarily via hydride ion transfer reactions such as,



3) The ions remaining after ion molecule reactions undergo neutralization. The neutral species so formed are highly excited and are assumed to decompose into a hydrogen atom and the corresponding radical or molecule.

4) Disproportionation and combination are the only reactions of the radicals formed in 1), 2), and 3).

5) The G-values of products produced in steps 1) to 4) are calculated by summing the number of molecules of each product formed per 100 ions and dividing this quantity by the value of W for the parent compound.

The agreement between the measured yields from the n-pentane radiolysis and the calculated yields from the mass spectrum were surprisingly good. There are a number of objections to the above method, the most serious one being that in the normal mass spectrometer the parent molecule ion has  $10^{-6}$  to  $10^{-5}$  seconds to decompose before undergoing a collision. In gas phase radiolysis at near atmospheric pressure, on the other hand, the molecule ion has only approximately  $10^{-10}$  seconds to undergo fragmentation before making a collision. The competition between fragmentation and reaction of the parent ion at one





atmosphere pressure, has been investigated by Stevenson (45). He concluded that for propane and higher hydrocarbons, dissociation could compete with ion molecule reactions. A second objection is that only hydride-ion transfer reactions have been considered. There are other exothermic or thermoneutral ion-molecule reactions, such as proton transfer and condensation reactions, which can lead to alterations in the product yields. A third objection is that the calculation does not include formation of non-ionized excited species which can give rise to radiolysis products. The presence of products resulting from non-ionic processes has recently been demonstrated by radiolysis studies in the presence of electric fields (46).

Recent work in high pressure mass spectrometry, where ion source pressures in the 1-2 Torr range (47) and even up to 200 Torr (48) have been achieved, are directly related to gas phase radiolysis studies. This field promises to yield a great deal of information that can be used in sorting out the complex mechanisms involved in vapor phase radiolysis of hydrocarbons.

## 2. Methods of Study Used in Gas Phase Radiolysis

### a) Pure Substrate Radiolysis

The first step in a complete radiolysis investigation is determination of the overall decomposition pattern of the compound. This involves the radiolysis of the pure vapor at a fixed pressure and temperature. The various product molecules are identified and their

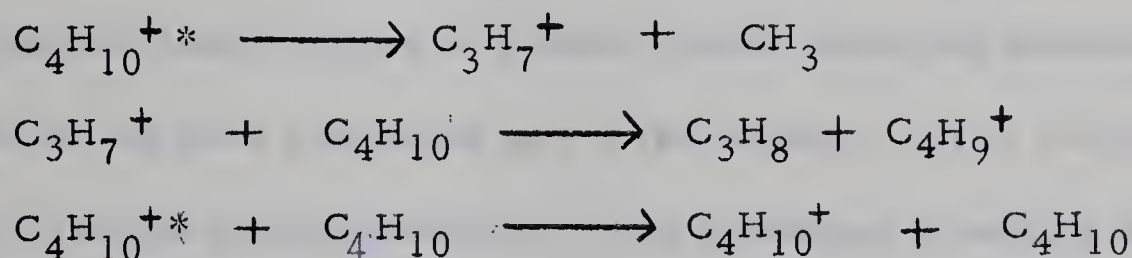




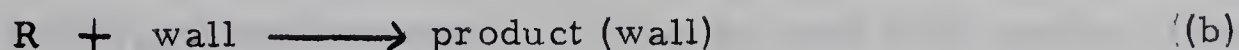
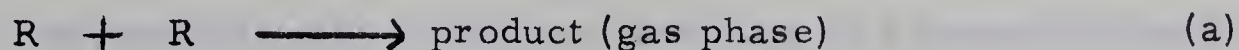
yields determined as a function of the total dose absorbed by the sample. In an attempt to obtain the initial decomposition patterns, free of secondary reactions, the dose dependent yields are extrapolated to zero dose.

The effects of temperature and pressure of the gas on product yields are often included in the study of the pure compound. The presence of unimolecular decompositions of excited molecules and ions in the radiolysis system can in principle be detected by pressure sensitive product yields.

This can be illustrated by the pressure effect observed in the radiolysis of n-butane (49). The decrease in the propane yield was attributed to collisional deactivation of the excited butane ion at high pressures, according to the following reaction scheme.



The effect of pressure can give evidence about the presence of a competition between gas phase and wall reactions.



As the pressure is decreased, diffusion of R to the wall is favored, and the product yield for reaction (a) would decrease.

Temperature does not affect the formation of reactive inter-



mediates produced as a result of the interaction of the radiation with the substrate. However, if an effective competition exists, reactions of these reactive species may exhibit a temperature dependence. The observed temperature dependence or independence of radiolysis product yields can be used as a criterion for possible mechanism of formation. The temperature effect on the radiolytic decomposition of diethyl ether (50) in the vapor phase was used to formulate a partial reaction mechanism.

b). Use of Additives

Small concentrations of compounds, which are specifically reactive towards either ions or radicals or some particular reactive species, are often added to the compound being studied. The basis for this technique is that the additive will react with all of one particular type of species; then changes of product yields observed between the radiolysis of the pure compound and of the mixture can be attributed solely to this type of intermediate. This technique of adding small concentrations of other compounds to the radiolysis system is referred to as scavenging. The added compounds are called scavengers.

In principle, the scavenger technique is a powerful tool for studying radiolysis mechanisms. It must be used with caution, however. There is difficulty in choosing a compound that will react with only one type of intermediate. Iodine, commonly used as a radical scavenger





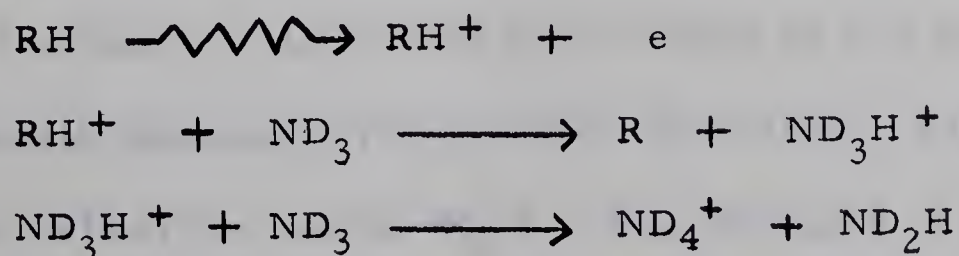


can also react with electrons to form an iodide ion and an iodine atom.



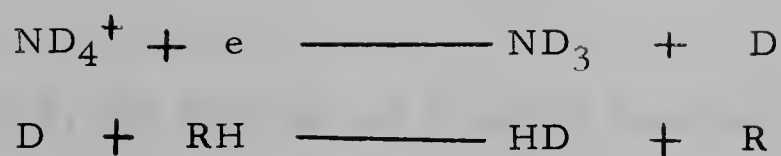
The neutralization reaction then changes from a positive ion-electron combination to a positive ion-iodide ion neutralization which can lead to the formation of different products. Further complications arise in the case of hydrogen iodide (51), which can react with both radicals and electrons, with the eventual formation of iodine. The iodine so formed then acts as a scavenger itself. Nitric oxide, which has been extensively used to suppress radical reactions in vapor phase radiolysis of alkanes, can also interfere with ionic reactions. Because its ionization potential (9.25 ev) is below that for most alkanes, charge transfer from the hydrocarbon positive ion to the nitric oxide can occur. In addition, nitric oxide can capture an electron to form a negative ion. It has also been shown that nitric oxide can act as a free radical chain initiator (52).

Ammonia or perdeutero-ammonia have been used as positive ion scavengers (53, 54). In the gas phase the use of this additive is apparently without complications. With perdeutero ammonia, the yield of scavengeable positive ions is determined by measuring the HD yield. The reaction scheme is









### c) Isotope Labelling Techniques

The radiolysis of deuterated or partially deuterated compounds is sometimes used to identify specific processes in the radiolysis mechanism. Ausloos (55) made use of equimolar mixtures of the fully deuterated and non-deuterated forms of a compound to differentiate between products formed by unimolecular and bimolecular reactions. Products arising from a unimolecular reaction are either fully deuterated or non-deuterated, whereas those products which result from a bimolecular reaction contain partial deuteration as well. Dyne and co-workers (34) have employed a similar technique but use a small variable concentration ( $\sim 1-5\%$ ) of the fully deuterated compound which acts as a detector molecule for unimolecular and bimolecular reaction products.

A combination of techniques 2) and 3) where either the parent compound or the scavenger is deuterated, is commonly used. The radicals formed during the radiolysis of deuterated propane were detected by the addition of  $\text{H}_2\text{S}$  (56). The  $\text{H}_2\text{S}$  scavenges the deuterated radicals by the reaction



where  $\text{R}_d$  represents a deuterated alkyl radical or a D atom. The yield of this partially deuterated product with one H atom is then measured to give the yield of the radical ( $\text{R}_d\cdot$ ). The product  $\text{R}_d\text{H}$  could conceivably



be formed by the hydride ion transfer reaction



but since this reaction is highly endothermic for alkyl radical ions,  $R_d$ , (19 kcal/mole for  $CH_3$  ; 79 kcal/mole for  $C_6H_{11}$  ) it is not likely to occur.

d) Radiolysis in the Presence of an Electric Field

The study of gas phase radiolysis in the presence of electric fields was pioneered by Essex and co-workers beginning in 1934 (57). Essex found that the yields of some products increased if an electric field in the saturation current region was applied during radiolysis. This increase in decomposition was attributed to collisions between electrons accelerated by the field, and the gas molecules (58). Because the electric field was in the saturation current region, the electrons did not gain sufficient energy from the field to cause ionization, so the increased decomposition was assumed to be due to the formation and subsequent reaction of neutral excited molecules. This effect of electric field has been used to identify products arising from neutral excited molecule decompositions in a number of recent investigations (46, 55, 59, 60). A basic assumption in this work was that fast ion-molecule reactions are unaffected by the electric field, so the yields of products arising from these reactions will remain constant in an increasing electric field, while the yield of products formed from excited molecules will increase with increasing field strength. Radical





reactions were suppressed by the presence of a radical scavenger.

### 3. Features and Reactions Observed in the Gas Phase Radiolysis of Alkanes

#### a) General Features

The major single product observed in the gas phase radiolysis of low molecular weight alkanes, at least up to  $C_7$  compounds is hydrogen. Two other prominent types of products are usually formed. The larger of these is the parent olefin, such as cyclohexene from cyclohexane; the other consists of the dimer of two parent radicals. The dimer product is butane in the case of ethane radiolysis, or dicyclohexyl from the radiolysis of cyclohexane. In addition to these two types of product, there are a number of other products formed, both saturated and unsaturated. These include compounds of molecular weight both less than and greater than the molecular weight of the parent material. In general, of the products measured, those with molecular weights less than the parent molecule are produced in larger yields than are products of molecular weight greater than the parent compound. For instance, in the radiolysis of cyclohexane vapor with  $\gamma$ -rays (21, 61) the yields of ethane and ethylene are approximately equal to the cyclohexene yield and so rank as major products. The existence of a high molecular weight polymeric product has frequently been suggested, but there are few quantitative measurements of its yield (20).

An important feature of the radiolysis of alkanes in the gas phase is the occurrence of secondary reactions between radiolysis products and reactive intermediates present in the system during radiolysis. This





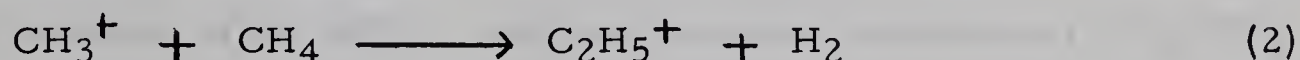
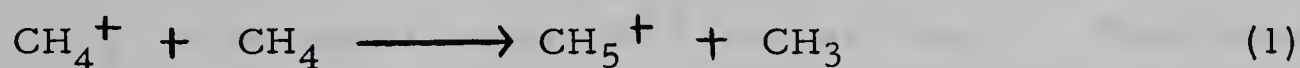
feature was discussed previously and will not be repeated here.

Because the products formed in the radiolysis of these systems range all the way from hydrogen to polymers, complex mechanisms are necessary to explain the overall radiolysis.

b) Reactions Observed

Ionic processes will be considered first.

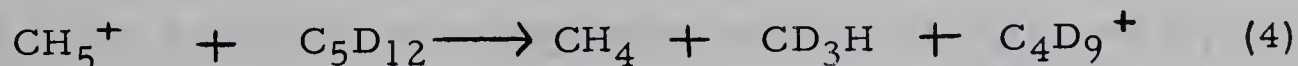
The following ion-molecule reactions have been deduced from the mass spectrum of methane at 2 Torr (47) and are postulated to occur in the gas phase radiolysis of methane (20, 60, 63).



Reaction (2) was suggested as a contributor to the yield of hydrogen that was unscavengable by a radical scavenger. Ausloos et al (64) found that the yield of  $\text{C}_2\text{H}_5^+$  decreases with increasing pressure of methane, which indicated that at high pressure reaction (1) was favored over the fragmentation reaction (3).



Proton transfer from  $\text{CH}_5^+$  to the higher hydrocarbons such as propane, butane, and pentane was observed in the radiolysis of mixtures of methane with these compounds (65). The protonated hydrocarbon rapidly decomposes into a carbonium ion and a neutral molecule. The reaction scheme suggested for methane-pentane mixtures was





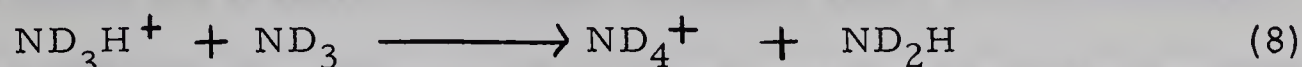


Reaction (4) was found to be the most important while reaction (6) was of relatively minor importance.

The proton transfer reaction from  $\text{CH}_3^+$ ,  $\text{CH}_4^+$ ,  $\text{CH}_5^+$ , and  $\text{C}_2\text{H}_5^+$  to  $\text{ND}_3$  has been observed by Munson and Field (66) in the ion source of a mass spectrometer at 2 Torr pressure.



They estimated the rate constant for the reaction (7) with RH equal to  $\text{CH}_5$  or  $\text{C}_2\text{H}_5$ , to be approximately  $10^{13} \text{ l-moles}^{-1}\text{sec}^{-1}$ . They found that the intensity of the  $\text{ND}_3\text{H}$  peak in the mass spectrum of  $\text{CH}_4\text{-ND}_3$  mixtures goes through a maximum and then decreases with increasing ion source pressure. At the same time the  $\text{ND}_4$  peak intensity increased continuously. The rate constant for the exchange reaction



was estimated to be approximately  $10^{12} \text{ l-mole}^{-1}\text{sec}^{-1}$ . The exchange reaction between  $\text{ND}_4^+$  and  $\text{CH}_4$  did not occur. Miyazaki and Shida (54) proposed similar proton transfer from  $\text{C}_3\text{H}_7^+$  to  $\text{NH}_3$  in the vapor phase radiolysis of n-butane.

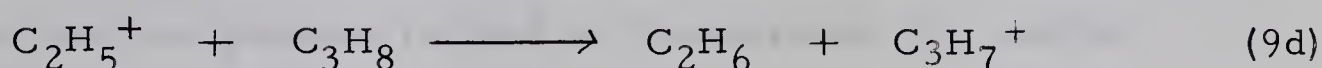
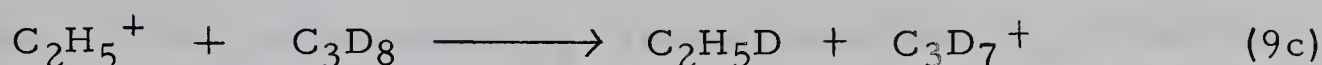
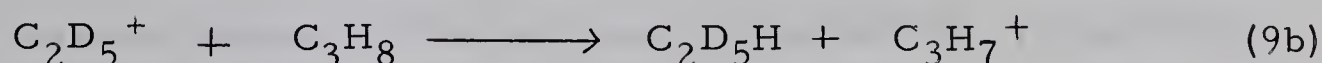
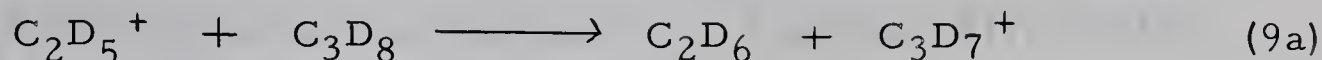
Hydride ion ( $\text{H}^-$ ) transfer reactions are known to occur (67) and have been extensively studied by Ausloos and co-workers (68) in the radiolysis of propane. From the isotopic composition of the ethanes produced in the radiolysis of an equimolar mixture of  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{D}_8$







in the presence of a radical scavenger, the following hydride ion transfer reactions were proposed.

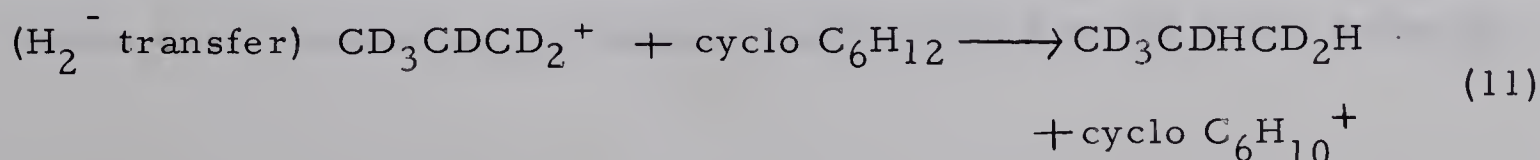


In a later study (69) of the radiolysis of propane in the presence of other added hydrocarbons, the relative rate of hydride ion transfer to the ethyl ion from RH compared to propane ( $k_{10}/k_9$ ) was measured.

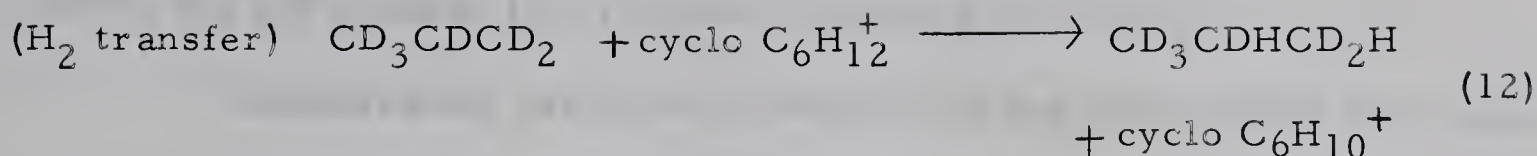


The value of the ratio  $k_{10}/k_9$  increased with increasing molecular weight of RH, and decreased with branching of the added hydrocarbon. Preference for removal of the hydride ion from a tertiary position was also noted. Hydride ion transfer reactions to propyl ions, in the radiolysis of n-butane (54) have been observed. These reactions are also suggested to occur with unsaturated ions such as  $\text{C}_2\text{H}_3^+$  (21) and  $\text{C}_3\text{H}_5^+$  (70) to form ethylene and propylene respectively. In general, hydride ion transfer reactions will occur for all ions if the reaction is exothermic (71).

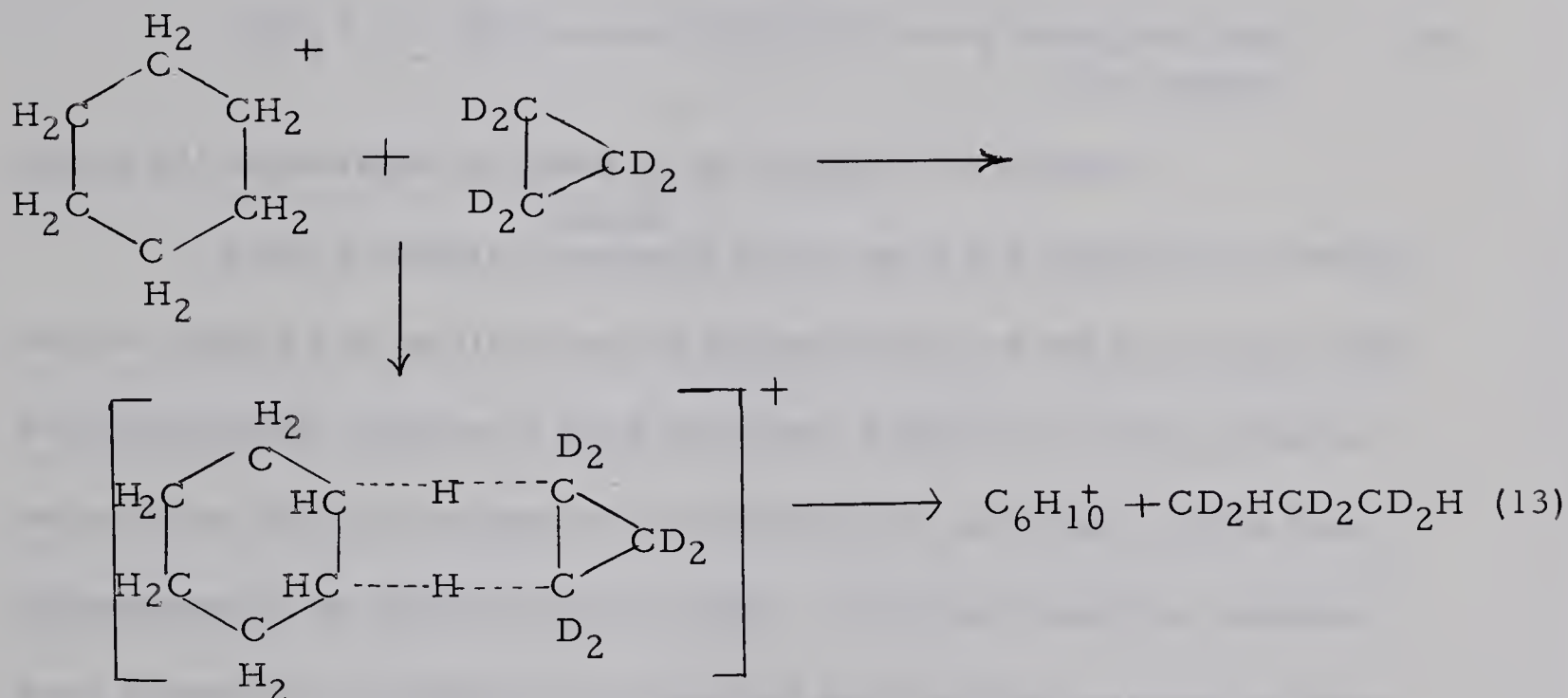
Two other ion-molecule reactions, which are related by reversing the charges on the two reactants, are the  $\text{H}_2^-$  and  $\text{H}_2$  transfer reactions between an alkane and an olefin. The following reactions have been shown to occur (72, 73)







where  $\text{CD}_3\text{CDHCD}_2\text{H}$  is formed exclusively. Reactions (11) and (12) were also observed where cyclohexane was replaced with cyclopentane or n-pentane. When cyclopropane- $\text{d}_6$  replaces propylene  $\text{d}_6$  in reaction (12) the predominant propane formed in the presence of a radical scavenger was  $\text{CD}_2\text{HCD}_2\text{CD}_2\text{H}$ . This was explained by the  $\text{H}_2$  transfer reaction



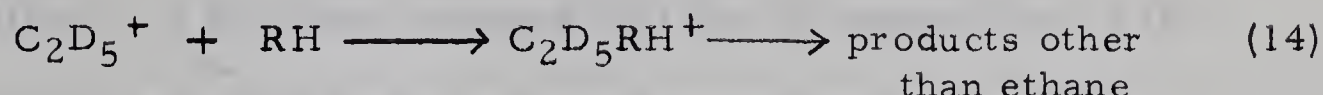
Transfer of  $\text{H}_2^-$  from a series of hydrocarbons to the  $\text{C}_3\text{D}_6^+$  ion was studied using cyclopentane- $\text{d}_{10}$  as the source of  $\text{C}_3\text{D}_6^+$ . For most saturated hydrocarbons the  $\text{H}_2^-$  transfer reaction occurred at similar rates. The rate, relative to cyclopentane, decreased with branching of the saturated hydrocarbon and for neo-pentane did not occur at all. It was suggested that the  $\text{H}_2^-$  transfer would not occur unless hydrogen atoms were present on two adjacent carbon atoms of the donor molecule.





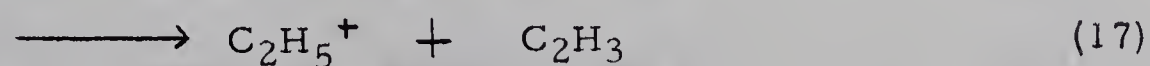
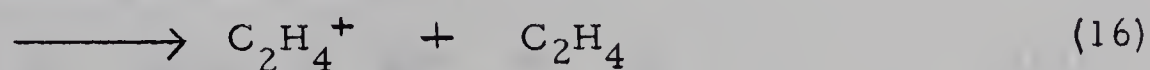
Olefins did not undergo  $H_2^-$  transfer reactions with  $C_3D_6^+$ .

Condensation reactions between ions and unsaturated molecules have been postulated to occur. In the above mentioned study of  $H_2^-$  transfer reactions, the olefins were postulated to undergo a condensation reaction with the  $C_3D_6^+$  ion. Lias and Ausloos (74) explain the reduction of the non-radical ethane yield observed with the addition of unsaturated and aromatic compounds to propane, by an addition reaction with the ethyl ion.



where RH represents an olefin or an aromatic compound.

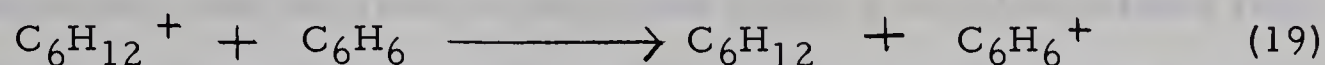
Some products have<sup>which</sup> been observed in the radiolysis of hydrocarbon vapors can be attributed to fragmentation of the parent ion (60). In an equimolar mixture of light and heavy substrate, these products were either fully deuterated or non-deuterated, and their yields were independent of an applied electric field. This indicated the products were formed by a unimolecular reaction and that the precursors were ionic. Interference from radical reactions was eliminated by the presence of a radical scavenger in the system. The fragmentation of the cyclobutane ion was shown to consist of the following processes (60).







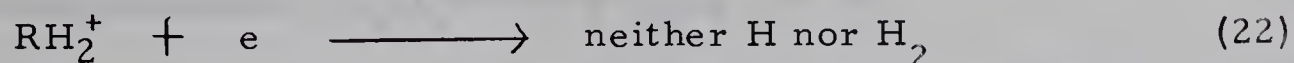
If the radiolysis system contains an additive or a radiolysis product with an ionization potential lower than that of the substrate molecule, then charge transfer from the substrate ion to the molecule of lower ionization potential can occur. Charge transfer from  $C_6H_{12}^+$  to benzene in  $\alpha$ -particle radiolysis of cyclohexane-benzene mixtures (75) has been suggested.



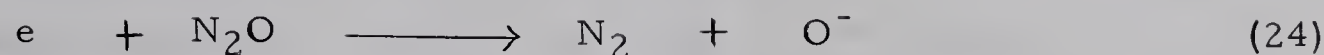
The role of ion neutralization in gas phase radiolysis is not well understood. It has been assumed (43) that decomposition of the excited molecule produced by ion-electron neutralization yields a hydrogen atom and the corresponding radical.



The species taking part in the neutralization process can be changed by the addition of electron scavengers. Ion-electron neutralization is replaced by ion-ion neutralization. The effect of changing the neutralization process in this way was shown by the addition of nitrous oxide to propane (76). The hydrogen yield was smaller in the presence of nitrous oxide than in pure propane radiolysis. The difference in yield was ascribed to formation of a H atom in an ion-electron neutralization, but not in an ion-ion neutralization. The following reaction sequences were proposed by Johnson & Warman (29).



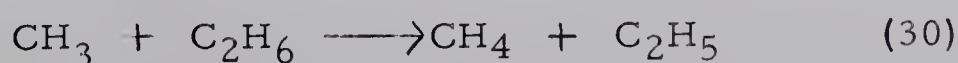
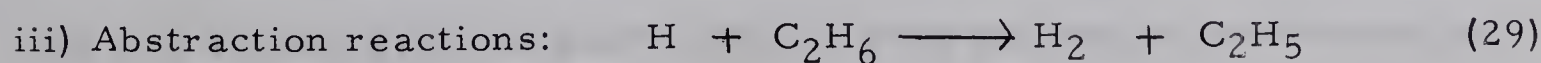
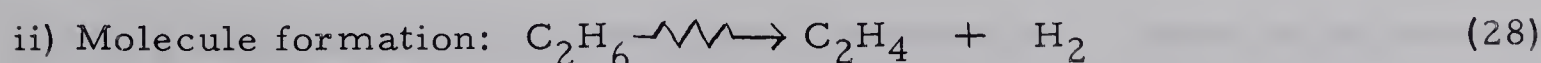




from the decrease of the hydrogen yield ( $-\Delta G(\text{H}_2) = 2.6$ ) in the presence of nitrous oxide, and the yield of electrons ( $G(\text{e}) = 4.3$ ) (calculated from the W-value for propane) they concluded that approximately 60% of the neutralization in pure propane gives rise to hydrogen atoms.

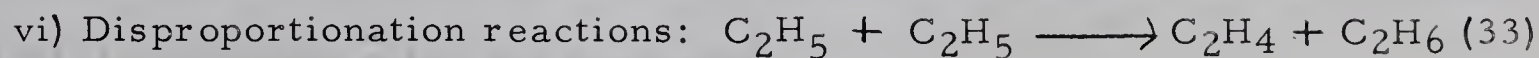
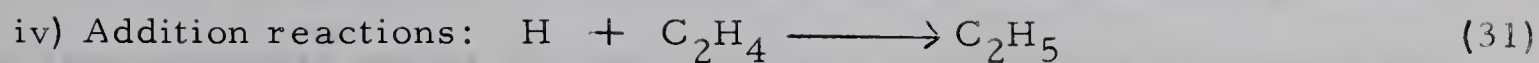
Free radicals have long been postulated as intermediates in the radiolysis of gaseous alkanes. Indirect evidence for their existence comes from scavenger studies, where the yields of certain products are inhibited by the addition of known radical scavengers. There are no direct observations of radicals in the radiolysis of gaseous alkanes, although in the liquid phase, alkyl radicals produced by electron irradiation have been observed by E.S.R. techniques (77). Radicals can be formed by the fragmentation of the parent ion, as illustrated previously for cyclobutane, and from decomposition of a neutral excited molecule.

Some different types of free radical reactions can be illustrated by reactions postulated by Yang & Gant in the radiolysis of ethane (78).









The butane yield in the above study was found to decrease with increasing dose. The explanation put forward was that radicals formed in reaction (31) were "hot" ethyl radicals which reacted before they were thermalized. Radicals formed with more kinetic energy or excitational energy than the average thermal energy of the surroundings are said to be "hot" (79). The disproportionation to combination ratio for "hot" radicals is higher than for thermal radicals thus favoring reaction (33) over reaction (32). "Hot" radicals are also produced by decomposition of the excited molecule formed in a neutralization process. "Hot" propyl radicals will dissociate at room temperature

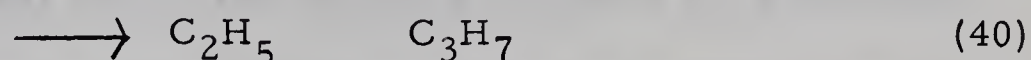
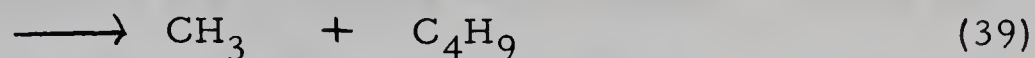
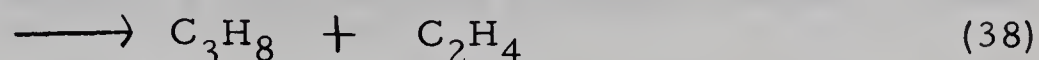
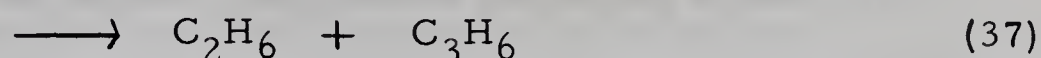
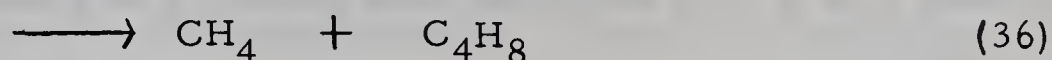
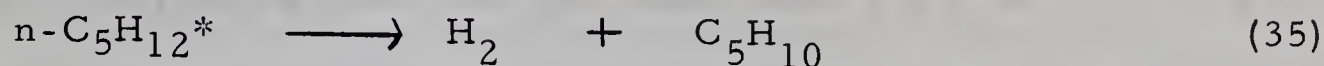


while thermal propyl radicals are stable (79).

The decomposition of neutral excited molecules into stable products are also postulated in gas phase systems. However their contribution to the overall decomposition is still a subject of speculation. These unimolecular decompositions have been identified by a technique similar to those used to isolate parent ion decompositions. From an equimolar mixture of light and heavy substrate such products have either the fully deuterated or non-deuterated composition. Their yields increase with an increasing applied electric field in the saturation current region.



The modes of decomposition of neutral excited molecules for a number of low molecular weight alkanes have been investigated by Ausloos and coworkers (42, 46, 55, 59, 60, 64). For the decomposition of n-pentane (55) the following paths are suggested.



The  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$  radicals produced in reactions (39) and (40) may be "hot" and could perhaps decompose further.

It is of interest to know the relative contributions of these ionic, radical, and excited molecule processes to the overall decomposition of the compound under irradiation. This unfortunately is very difficult since the same products can arise from each process. Radicals can be formed both in ion molecule reactions, ion fragmentation, and excited molecule decomposition.

#### E. PREVIOUS WORK ON THE RADIOLYSIS OF METHYLCYCLOHEXANE

The only previous study on methylcyclohexane vapor was the  $\alpha$ -particle radiolysis at  $108^\circ\text{C}$  by Ramaradhya (80). This was an incomplete study in that only gaseous products were measured. The gases volatile at  $-196^\circ\text{C}$  contained mainly hydrogen with about 4% methane.

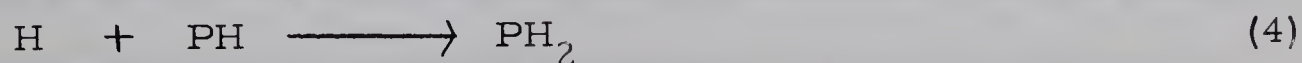
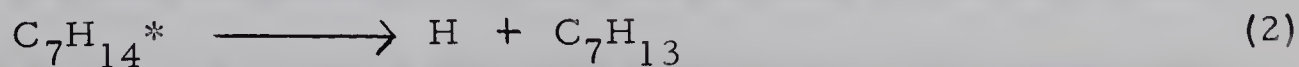




The total gas non-condensable at  $-196^{\circ}\text{C}$  ( $G(-196^{\circ}) = 6.1 \pm 0.2$ ) was independent of dose from  $0.2$  to  $11.7 \times 10^{19}$  ev/g. The yield of the  $-112^{\circ}\text{C}$  fraction of gaseous products decreased rapidly from  $G = 4.0$  to  $G = 1.3$  with increasing dose over the range from  $0.2 \times 10^{19}$  to  $1.2 \times 10^{19}$  ev/g. This was followed by a further slow decrease to  $0.9$  at a dose of  $11.7 \times 10^{19}$  ev/g. The various components contained in the  $-112^{\circ}\text{C}$  gas fraction were not measured quantitatively although methane, ethane, ethylene, propane, acetylene and propylene were present. Under the analytical conditions that were used no liquid products were detected, even though liquid products from cyclohexane vapor radiolysis under similar conditions were observed (80, 81). The  $G(-196^{\circ})$  from methyl cyclohexane mixtures was measured as a function of concentration of added benzene, and of added cyclohexene.

The methylcyclohexane results were treated according to the same two mechanisms used for interpreting the results from the radiolysis of cyclohexane vapor (75); a scavenging mechanism and an energy transfer mechanism. These two mechanisms are outlined below.

(1) Scavenging Mechanism

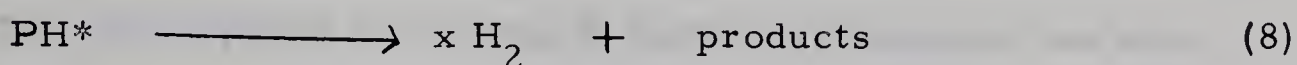
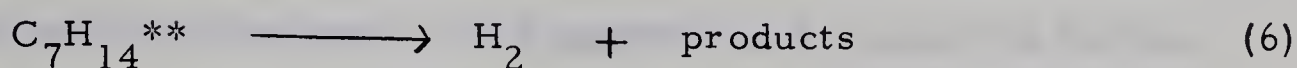
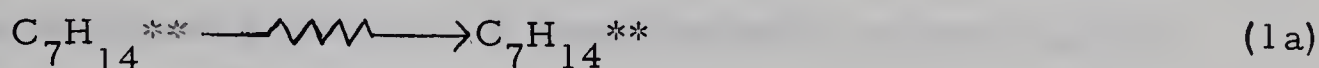






In reactions (4) and (5), PH refers to either benzene or cyclohexene, and  $\text{PH}_2$  and P, to the radicals formed by hydrogen atom addition, and abstraction, respectively. A steady state kinetic analysis of this mechanism, assuming  $G(-196^\circ) = G(\text{H}_2)$  was made. The values of  $k_5/k_3 = 3 \pm 3$  for the methylcyclohexane-benzene mixture and  $> 5$  for the mixture with cyclohexene were obtained. The ratio  $k_4/k_3$  was  $2.6 \pm 0.2$  with added benzene and  $> 9$  with added cyclohexene.

## (2) Energy Transfer Mechanism



where  $0 \leq x \leq 1$ .

The steady state kinetic treatment of this energy transfer mechanism yielded  $k_7/k_6 = 1000 \pm 800$  l/mole when benzene was added and  $\approx 1500$  l/mole (within a factor of 2) for cyclohexene additive.

Because of the lack of precision in the experimental data no decision was made favoring either of the two mechanisms. However in the cyclohexane vapor radiolysis the scavenging mechanism was rejected as the sole mechanism. This was because of the high value obtained for  $k_5/k_3 = 2.5$  which indicated abstraction of hydrogen from benzene was favored over abstraction from cyclohexane. In the energy transfer mechanism for cyclohexane radiolysis, the species formed in



reaction (1a) was suggested to be a positive ion, and reaction (6) represented the dissociative recombination of the ion and the electron. The possibility of both mechanisms being operative in cyclohexane vapor was proposed. The same considerations may also apply to the methylcyclohexane system.

The failure to observe liquid products from the methylcyclohexane vapor radiolysis was surprising. In the cyclohexane system (60) the occurrence of a polymerization reaction (60) was postulated to account for the non-detection of approximately seven out of a total of eight G units of hydrogen-deficient products. A more extensive polymerization reaction in methylcyclohexane was suggested as a reason for the low yields of liquid products.

The liquid phase radiolysis of methylcyclohexane has been included in several survey-type investigations (82-86) however the only detailed study of it was by Freeman (87, 88). He studied the pure methylcyclohexane radiolysis as well as solutions of methylcyclohexane with benzene. The hydrogen and methane yields from pure methylcyclohexane and from mixtures with benzene have also been measured by Merklin and Lipsky (89).

The major products observed by Freeman from the radiolysis of pure methylcyclohexane were hydrogen ( $G = 4.80$ ); 1-methylcyclohexene plus methylenecyclohexane ( $G(1\text{-MC} + \text{MEC}) = 2.65$ ); 3- plus 4-methylcyclohexene ( $G(3\text{-} + 4\text{-MC}) = 0.83$ ); two open chain heptenes ( $G = 0.33$  and  $0.31$ ); bi-methylcyclohexyl ( $G(\text{BMC}) = 0.75$ ); and methylcyclohexyl



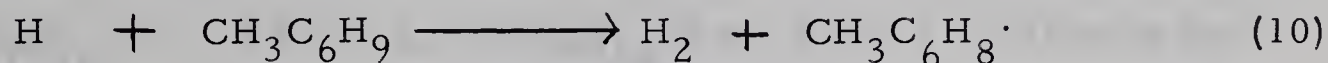


heptene (  $G(\text{MCHH}) = 0.013$ ). The  $G$  values were those obtained by extrapolation to zero dose. Other minor products were methane ( $G = 0.08$ ) and  $\text{C}_2\text{-C}_4$  gases (total  $G = 0.1$ ). Merklin and Lipsky reported a much higher hydrogen yield,  $G = 6.25$ .

The yields of all major products decreased with increasing dose. The 1-MC + MEC and BMC yields were more severely affected than was that of hydrogen. The hydrogen yield decrease was explained by hydrogen atom scavenging by olefin



The olefin decrease was attributed to three processes; reaction (9) above, along with the abstraction reaction



and an olefin polymerization reaction involving mainly the methylene-cyclohexane isomer. The reduction of the BMC yield was suggested to be due to reaction (10) since it did not form methylcyclohexyl radicals. Merklin and Lipsky also ascribed the dose effect on the hydrogen yield to hydrogen atom scavenging by olefins (89).

When benzene was added to liquid methylcyclohexane the yields of the major radiolysis products decreased rapidly with increasing benzene concentration up to approximately 5%, and then more slowly as the benzene concentration was increased further. This behavior was explained by postulating two reactive species ( $\text{C}_7\text{H}_{14}'$  and  $\text{C}_7\text{H}_{14}''$ ) present in the methylcyclohexane radiolysis system which react with



benzene at different rates.

Two mechanisms were proposed, one for the high and one for the low benzene concentration region. The mechanism proposed for the high benzene concentration region involved energy transfer from the reactive species,  $C_7H_{14}''$ , to benzene. This active species was either a positive ion or an excited molecule. It was suggested that in the low benzene concentration region the benzene acted as a hydrogen atom scavenger. The hydrogen atoms were formed from the decomposition of the second major reactive species  $C_7H_{14}'$ . These mechanisms were used in a kinetic analysis of the hydrogen yield to obtain the yields of the two reactive species in pure methylcyclohexane. The values found were  $G(C_7H_{14}') = 1.8 \pm 0.3$  and  $G(C_7H_{14}'') = 3.0 \pm 0.3$ . Merklin and Lipsky (89) calculated the yields for the corresponding species  $C^{\ddagger}$  and  $C^*$  to be  $G^{\ddagger} = 1.4 \pm 0.4$  and  $G^* = 4.8 \pm 0.3$  respectively. The agreement between  $G(C_7H_{14}')$  and  $G^{\ddagger}$  is quite good. The discrepancy between  $G^*$  and  $G(C_7H_{14}'')$  results from the different total hydrogen yield that was obtained in the two investigations.

Thus in the radiolysis of liquid methylcyclohexane there is evidence for the formation of two reactive species that are precursors of hydrogen.

#### F. EXTENT OF PRESENT STUDY

The present investigation of the radiolysis of methylcyclohexane vapor was undertaken to obtain more detailed information about





the factors affecting product yields in the gas phase radiolysis of alkanes. Equipped with such information, it may then be possible to begin to sort out the complex maze of reactions that occur in these systems.

To obtain detailed information on the factors which affect the product yields, methylcyclohexane vapor was irradiated under a variety of conditions, and in a number of different mixtures. Pure methylcyclohexane radiolysis was studied as a function of dose, as a function of temperature, and as a function of pressure. Mixtures of methylcyclohexane with a number of scavengers were irradiated. The scavengers include ethylene, carbon tetrachloride, nitrous oxide, sulfur hexafluoride, perdeutero ammonia, and deuterium iodide. In the methylcyclohexane-nitrous oxide mixtures were greatly enlarged yields of some products where observed, temperature and pressure studies were done at fixed nitrous oxide concentrations. The examination of mixtures was extended to include competition studies between two of the above mentioned scavengers in methylcyclohexane. Competition studies between DI and  $C_2H_4$ ; DI and  $SF_6$ ; DI and  $N_2O$  as well as between  $N_2O$  and  $SF_6$  in methylcyclohexane were carried out.

Apart from the determination of product yields, the W-value for methylcyclohexane vapor was measured under the conditions used in the radiolysis study.





## EXPERIMENTAL

### A. Materials Used for Radiolysis

#### 1. Methylcyclohexane (MCH)

The material used was Phillips Petroleum Co. research grade, lot no. 1039, stated purity 99.92 mole percent. This material was further purified by one of the two following methods.

1) The MCH (500 ml) was shaken with 300 ml portions of concentrated sulfuric acid, the acid being changed every 12 hours until the appearance of yellow color in the acid layer after 4 to 5 hours shaking was slight. (Complete absence of yellowing in the acid layer was not achieved). The MCH was then washed several times, first with double distilled water (3 times), then with dilute  $\text{Na}_2\text{CO}_3$  solution, and again with double distilled water (5 times). Washing was followed by drying over anhydrous magnesium sulfate. The dried MCH was distilled through a column packed with glass helices; the middle half was collected, boiling point  $98^\circ$  at 700 mm. This fraction was degassed and stored in a reservoir closed with a Viton A greaseless stopcock, (G. Springham & Co.) under vacuum.

2) The second method of purification was a modification of the Vinogradov method (90). The MCH (500 ml) was shaken for 3 periods of one minute each with 150 cc of a 1:1 mixture of concentrated sulfuric and nitric acids. The MCH developed a yellow color. This yellow color disappeared on washing eight times with 200 ml portions of



concentrated sulfuric acid. The MCH was then washed with double distilled water, dilute  $\text{Na}_2\text{CO}_3$  solution, dried and distilled as in the previous method.

## 2. Carbon Tetrachloride

Eastman's Spectro grade carbon tetrachloride (Lot # 47A) was further purified by distillation through a column packed with glass helices. The middle half was retained, boiling point  $74^\circ\text{C}$ . The purified material was collected and stored in a glass stoppered bottle.

## 3. Nitrous Oxide

The nitrous oxide was obtained from Matheson & Co. The nitrous oxide was subjected to several trap to trap distillations at  $-196^\circ\text{C}$ , in the vacuum line. The nitrous oxide was pumped on during the distillation and then condensed into a storage reservoir on the filling line of the vacuum system.

## 4. Sulfur Hexafluoride

Sulfur hexafluoride from Matheson Co. was purified in the same manner as the nitrous oxide.

## 5. Perdeutero Ammonia

The  $\text{ND}_3$  was prepared by reaction of  $\text{D}_2\text{O}$  (Atomic Energy of Canada 99.7% D) with magnesium nitride following the procedure of Walker (91). About 40 grams of finely ground anhydrous magnesium nitride (Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio) was placed in a 30 cc stainless steel bomb, fitted with a





Hoke valve, in a dry box. The bomb was reassembled inside the dry box and then attached to the high vacuum system which had previously been equilibrated with  $D_2O$ . The magnesium nitride was degassed by pumping on it while heating the bomb to red heat. The degassing was continued until there was only a slight increase in pressure upon warming the bomb from room temperature to red heat. One ml of degassed  $D_2O$  was then distilled onto the magnesium nitride and allowed to remain in contact with the nitride for 24 hours. The  $ND_3$  formed was then distilled from the bomb and dried by distillation through two traps at  $-72^\circ C$  (dry ice-ethanol).

The isotopic purity of the resulting  $ND_3$  was estimated by measuring the isotopic composition of the hydrogen formed from the radiolysis of the  $ND_3$ . Assuming no isotope effect the  $ND_3$  was found to contain 95 atom percent D. Since an isotope effect would probably favor formation of H rather than D the estimated purity represents a lower limit.

## 6. Deuterium Iodide

The DI was prepared by direct reaction of deuterium and iodine at  $485^\circ C$  (92). The apparatus consisted of a 500 ml reaction vessel attached to a train of two traps via a greaseless Republic valve, a 250 ml storage bulb for the DI, also closed with a Republic valve, and a manometer. The line was attached to the high vacuum manifold and equilibrated with  $D_2O$  before preparation of the DI.



Analar reagent grade iodine (3.5 g) was placed in the bottom of the first trap and degassed from liquid nitrogen. The iodine was then distilled into the 500 cc reaction vessel. Deuterium (Matheson of Canada Co., Whitby, Ontario) was let into the reaction vessel to a pressure of 34 cm Hg. The Republic valve on the reaction vessel was closed and the reaction vessel was heated to  $485^{\circ}$  in an electric furnace for twenty hours. The DI was separated from the  $I_2$  by distillation through a dry ice-ethanol bath several times. The DI was then distilled into the 250 cc storage bulb.

As with  $ND_3$ , a sample of the DI was irradiated and the resulting  $D_2$ , HD and  $H_2$  measured. From the relative amounts of these hydrogens the DI was estimated to contain 96 atom percent D.

## 7. Ethylene

Phillips research grade ethylene (lot #954) with stated purity 99.92 mole % was degassed by trap to trap distillation. The receiver trap was pumped on during the distillation.

### B. Preparation of Samples

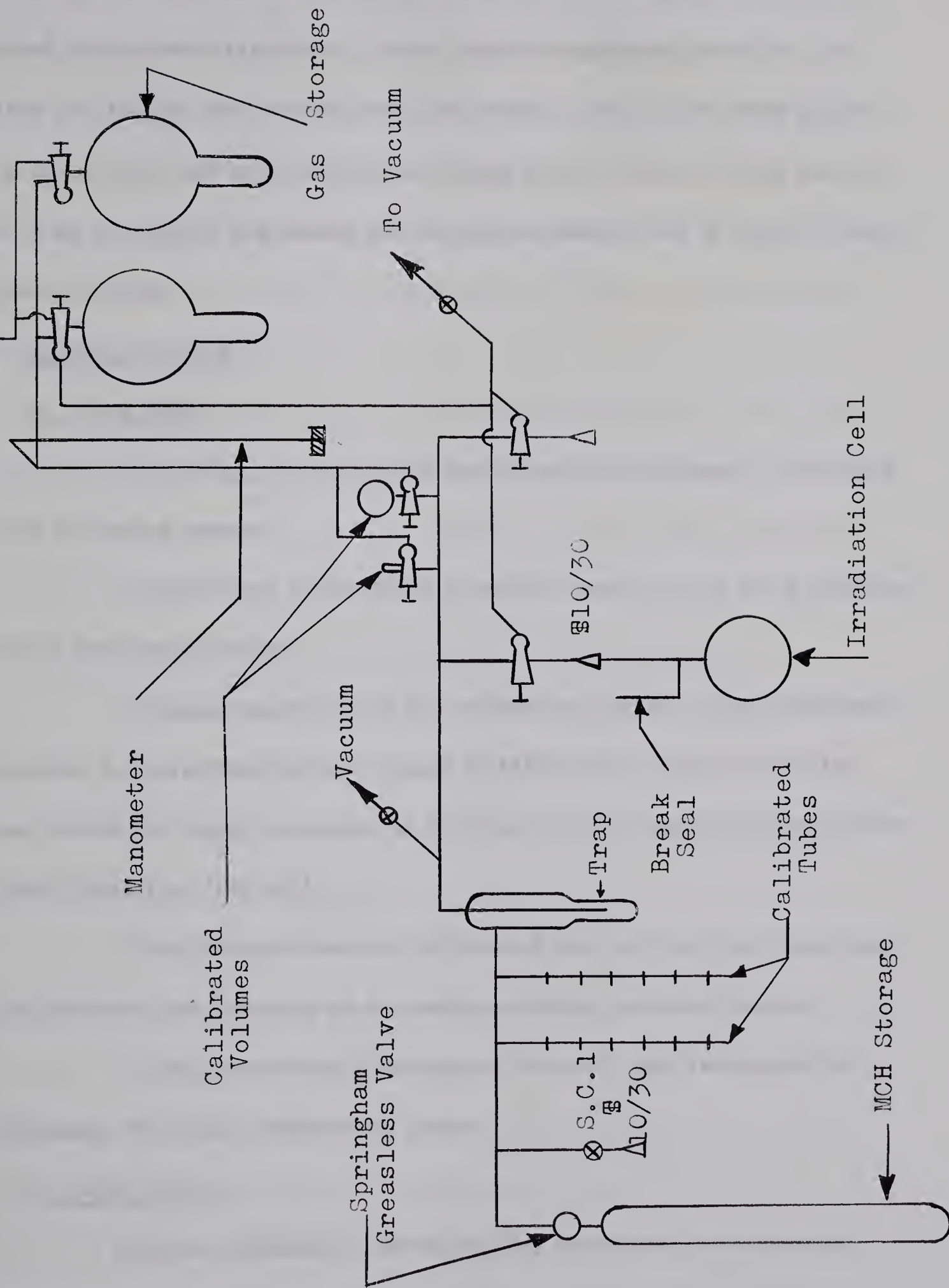
#### 1. Preparation of Cells

Irradiation cells were made from 500 ml round bottom flasks from which the necks were removed and replaced by a breakseal and a filling tube. The filling tube was attached to the filling line of the vacuum system through a 10/30 ground joint. (See Figure II-1).

The cells were cleaned with a 3:1 mixture of hot concentrated

FIGURE II-1Filling System

# To Gas Storage & Purification System







sulfuric and nitric acids. After the acid treatment the cells were rinsed in turn with tap water, dilute sodium carbonate solution, tap water and finally with double distilled water. The cells were dried in a clean oven and attached to the filling line. On the filling line the cell was evacuated and baked out at approximately  $500^{\circ}\text{C}$  for 2-3 hours prior to filling.

## 2. Filling of Cells

### a. Pure MCH

The filling procedure for pure methylcyclohexane consisted of the following steps:

- distillation of the MCH from the reservoir to the calibrated tube at ice temperature;
- measurement of the the volume of liquid in the calibrated tube with a correction for the amount of MCH in the vapor above the tube, using the vapor pressure of MCH at  $0^{\circ}\text{C}$  (11 mm) and the volume of the filling line (180 ml);
- distillation from the calibrated tube to the trap immersed in liquid nitrogen pumping on the sample during the distillation;
- distillation from the trap to the cell, and sealing off by collapsing the filling tube with a flame.

### b. MCH- $\text{CCl}_4$

For the irradiation of MCH- $\text{CCl}_4$  mixtures the following procedure was used:



- the desired concentration of  $\text{CCl}_4$  in MCH was made up by weighing the components into a small covered vial;
- the vial was attached to the filling line via a 10/30 ground joint at stopcock #1 and frozen with liquid nitrogen.
- the mixture was degassed three times from liquid nitrogen and three times from a MCH slush bath ( $-126^\circ\text{C}$ ) using the freeze, pump, melt technique;
- after degassing the mixture was distilled into the trap, pumping on it during the distillation;
- the remainder of the procedure was as for pure MCH radiolysis.

#### c. MCH plus Gaseous Additives ( $\text{N}_2\text{O}$ , $\text{SF}_6$ , $\text{ND}_3$ , DI)

For the addition of these additives to MCH calibrated volumes attached to the filling line were filled to a known pressure with the gas from a storage bulb and the additive was distilled into the cell.

#### C. Irradiation of the Samples

The samples were irradiated at  $110 \pm 5^\circ\text{C}$ . Heating of the samples was accomplished by means of a special heating mantle which encased the cell completely. The temperature was regulated by means of a variable transformer, and was measured with a thermocouple placed between the cell and the heating mantle.

The samples were irradiated in a 12,600 curie Gammacell 220 obtained from Atomic Energy of Canada Ltd. The cell was placed





in an aluminum frame which could be reproducibly positioned in the drawer of the source. Electrical and thermocouple leads were brought to the cell through the top of the Gammacell.

#### D. Analysis of the Samples

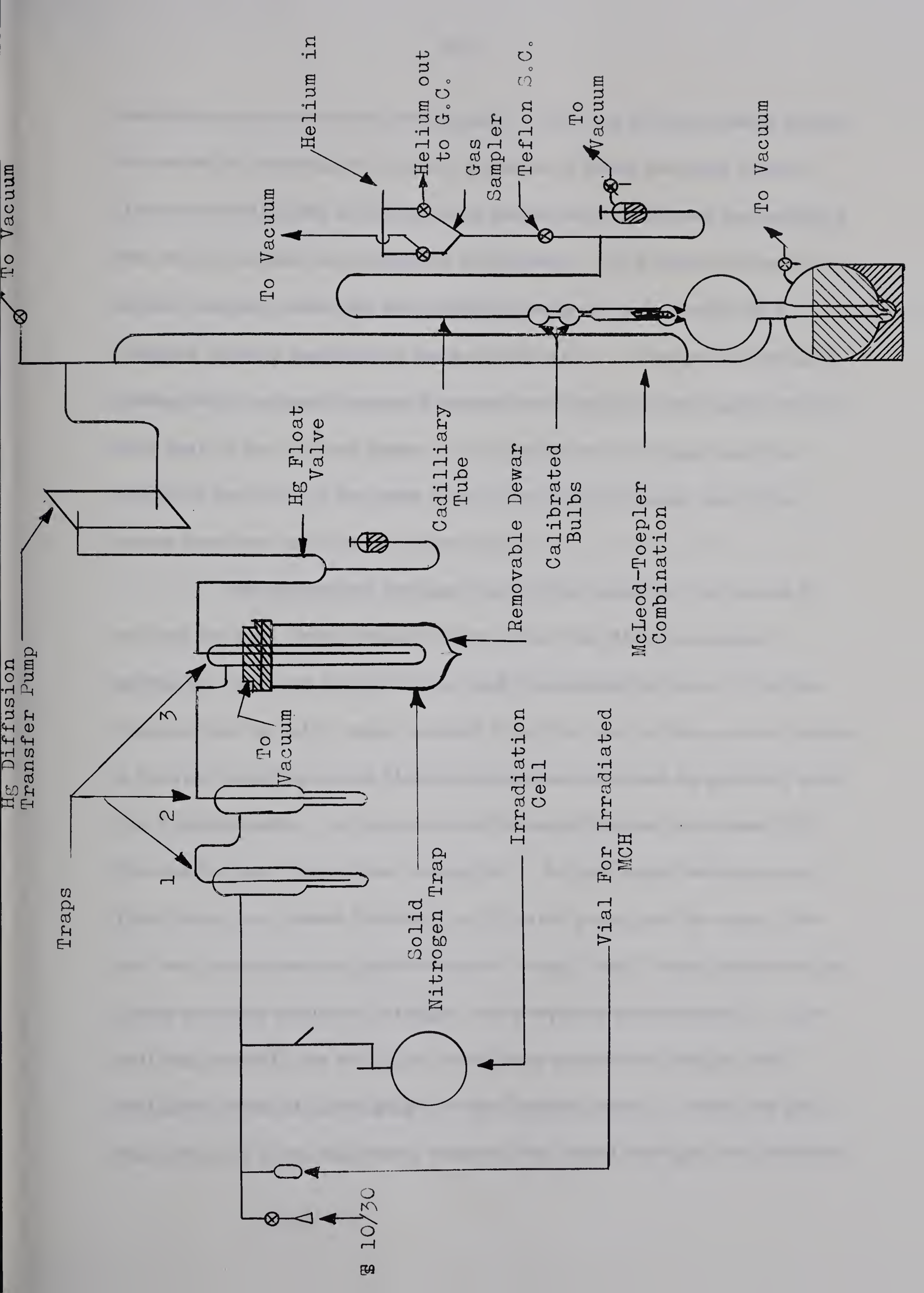
##### 1. Gaseous Products

The gaseous products were separated from the irradiated MCH by fractional distillation. The sample was passed through a series of traps kept at a low temperature such that the MCH and liquid products were condensed in a trap while the gaseous products passed through the traps to the collection system. The gaseous products were collected in two fractions, those volatile at  $-210^{\circ}\text{C}$  and those volatile at  $-112^{\circ}\text{C}$ .

The analysis line of the vacuum system is shown in Figure II-2. The line consisted of a series of three traps one of which was equipped for the preparation of solid nitrogen. Between the traps and the McLeod gauge- Toepler pump combination was a small mercury diffusion pump to facilitate the transfer of gases from the cell to the McLeod- Toepler apparatus. From the McLeod- Toepler apparatus the gases were transferred directly to the column of the gas chromatograph (Burrell Kromo-Tog Flame Ionization Model K-7).

The McLeod- Toepler apparatus was used to collect and measure the total amount of gaseous products in each fraction. The volume of gas was defined by the space between the upper and lower

FIGURE II-2Gas Analysis System





mercury levels in the McLeod gauge. The size of this volume could be varied by varying the relative position of these mercury levels. The two small bulbs of the McLeod gauge were calibrated by weighing the amount of mercury required to fill them. The internal diameter of the capillary tube was calibrated by measuring the length of a weighed bead of mercury in the capillary tube. A length of capillary tubing with constant internal diameter was used for the construction of this part of the McLeod gauge. The pressure of the gas was the height of mercury in the open arm of the McLeod gauge above the lower mercury level in the closed arm.

The procedure for gaseous product analysis was begun by sealing the cell, and a small vial to collect the MCH plus liquid products, on to the analysis line, and evacuating the line. The line was pumped on until, when isolated from the rest of the vacuum system a constant reading on the McLeod gauge was obtained by pumping with the Toepler pump. In practice the McLeod-Toepler zero was  $10^{-2}$  Torr-ml of gas, which was negligible. At this stage the mercury float valve was closed between the diffusion pump and the traps, the cell was immersed in liquid nitrogen, traps 1 and 2 were immersed in liquid nitrogen and solid nitrogen was prepared around trap 3. The cell was opened, the mercury cut off was opened and the gas was collected in the McLeod gauge by the Toepler pump. After the gas was removed from the frozen sample, the liquid nitrogen was removed





and the sample allowed to distill into trap 1. Pumping with the Toepler pump was continued during the distillation. From trap 1 the sample was allowed to distill into trap 2. The amount of gas was measured after each distillation. After the distillation into trap 1, greater than 99% of the total gas volatile at  $-210^{\circ}\text{C}$  (solid nitrogen) was collected. The  $-210^{\circ}\text{C}$  fraction of the total gas consisted of hydrogen and methane. Solid nitrogen was necessary to hold back the ethylene when the mercury diffusion pump was used in the analysis line. After the gases were collected by the Toepler pump and measured they were transferred directly to the carrier gas stream of the gas chromatograph. The remainder of the gaseous products, the  $\text{C}_2\text{-C}_4$  hydrocarbons, were removed in a second distillation step at  $-112^{\circ}\text{C}$  (ethanol slush). The gases were measured and transferred directly to the chromatograph as before.

After removal of the gaseous products the remainder of the sample was distilled back into the small vial which was sealed with a flame and removed from the analysis line. This was used for analysis of the liquid products.

#### Hydrogen Chloride Analysis in the $\text{MCH-CCl}_4$ System

The hydrogen chloride formed in the  $\text{MCH-CCl}_4$  radiolysis was contained in the  $-112^{\circ}\text{C}$  fraction of the gaseous products. Since  $\text{HCl}$  is not detected by the flame ionization detector of the gas chromatograph its yield was estimated by absorbing the  $\text{HCl}$  out of the  $-112^{\circ}\text{C}$



fraction on solid KOH.

A small U-trap ending in a side-arm was attached through a stopcock to the gas analysis line. The U-trap was filled with KOH and the KOH degassed. The total  $-112^{\circ}\text{C}$  fraction, including the HCl was measured as previously described and then distilled through the KOH in the U-trap into the side arm. The liquid nitrogen was then removed from the side arm and the gases passed back through the KOH and were again collected and measured in the McLeod-Toepler apparatus. The difference between the total  $-112^{\circ}\text{C}$  fraction and the amount of gas remaining after passing through the KOH was taken as the HCl yield.

## 2. Liquid Product Analysis

The vial that had been removed from the gas analysis line was opened and a one microliter aliquot of the liquid was injected into the gas chromatograph (Burrell Kromo-Tog, Flame Ionization Model K-7) equipped with a suitable column for the analysis.

The liquid products in the  $\text{MCH-CCl}_4$  system were analysed on a Burrell Model K2 gas chromatograph equipped with a thermal conductivity detector containing Gow Mac W-2 filaments and a glass column. The reason for the change of instruments was that the methyl cyclohexyl chloride from the radiolysis of  $\text{MCH-CCl}_4$  mixtures was found to decompose to methylcyclohexene and HCl on the metal inlet system and column of the Burrell K7 chromatography that was normally used.







The various columns used for the different analyses are summarized in Table II-1.

### 3. Identification of Products

The chief method of identification was comparison of retention times of product peaks on the G. C. column with the retention times of known compounds. Where possible, the retention times were compared with authentic samples of the products.

In some cases the product peaks were trapped after elution from a G. C. column and submitted for mass spectrometry or infrared spectroscopy analysis to aid in the identification. The products found in the various systems are given in the results section.

### 4. Calibration of the Gas Chromatograph

#### a. Gaseous Products

Each of the gaseous products was calibrated individually. An amount of the gas to be calibrated was measured in the McLeod-Toepler apparatus so the number of micromoles of gas was known; this gas was transferred to the gas chromatograph through the gas sampler (Figure II-2) and the area of the resulting peak measured, using the peak height times width at half height method. This procedure was repeated for various amounts of gas so that a plot of micromoles of gas versus peak area was obtained. The range of this plot was made to correspond to the range of peak areas observed for the radiolysis product. This procedure was repeated for each of the product gases.



TABLE II-1

COLUMNS AND CONDITIONS FOR PRODUCT ANALYSIS\*

<u>Products Analysed</u>	<u>Column</u>	<u>Conditions</u>
CH <sub>4</sub>	Charcoal 2.5 m	30°C flowrate 40 ml/min
H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CH <sub>4</sub>	Molecular Sieve 13x 10 ft x 3/16" (thermal conductivity detector)	30°C flowrate 45 ml/min
C <sub>1</sub> - C <sub>4</sub>	Silica Gel (Medium Activity 2.5 m)	Temperature programed from 30° - 100° @ 10°C/min flowrate 25 ml/min
liquid products from pure MCH radiolysis and from MCH and gaseous additives	Silica Gel (2.5 m) medium activity modified with 2% Apieson N grease	Temperature programed from 30° - 250° @ 10°C/min flowrate 40 ml/min
	Mixed Column, 1.5 m of modified silica gel 1.0M of 10% Apieson N on firebrick	Temperature programed from 30° - 225° @ 8°C/min flowrate 40 ml/min
liquid products from MCH - CCl <sub>4</sub> system	Silicone Grease (F & M) 2.5 m hair pin on Burrell K - 2 with thermal conductivity detector	Temperature programed from 30° - 160° flowrate 120 ml/min
H <sub>2</sub> O from MCH-N <sub>2</sub> O system	Poropak Type Q 6 ft (thermal conductivity detector)	100°C flowrate 60 ml/min

\* Unless otherwise noted all analyses were done on Burrell K-7 using a flame ionization detector.





From the peak area for the product in the irradiated sample the number of micromoles of gas was read off the graph. These calibrations were found to change appreciably with time. It was thus necessary to calibrate before each series of samples was analysed. Example calibration plots are shown in Figure II-3.

#### b. Liquid Products

To calibrate the G.C. for liquid product analysis, synthetic solutions which contained compounds of the same identity to those found in the irradiated sample were used. Where product compounds were unavailable, hydrocarbons of the same carbon number were substituted. The calibration solutions were made up by weighing the product compounds into MCH followed by dilution with MCH until they covered the concentration range found in the irradiated samples. These calibration solutions were then injected into the gas chromatograph, interspersed with irradiated samples. The area percent of each product peak as measured from the chromatogram was plotted against the weight percent, giving a calibration plot. Example plots for 1-MC and n-tetradecane are shown in Figure II-4. From the measurement of the area percent in the unknown sample the weight percent was read from the calibration plot. The peak areas were measured by planimeter.

The G-value of the product was obtained from the following formula:

$$G_{\text{prod.}} = \frac{\text{wt \%} \times \text{wt. of sample (g)} \times 6.02 \times 10^{23} \text{ (molecules/mole)}}{(\text{molecular wt.})_{\text{prod.}} \text{ (g/mole)} \times \text{Dose (100 ev)}}$$



FIGURE II-3Typical Calibration Plots for Gaseous Products

A: Hydrogen (Thermal Conductivity Detector)

B: Methane (Thermal Conductivity Detector)

C: Methane (Hydrogen Flame Detector)

D: Ethane (Hydrogen Flame Detector)

E: Propane (Hydrogen Flame Detector)

F: Propylene (Hydrogen Flame Detector)

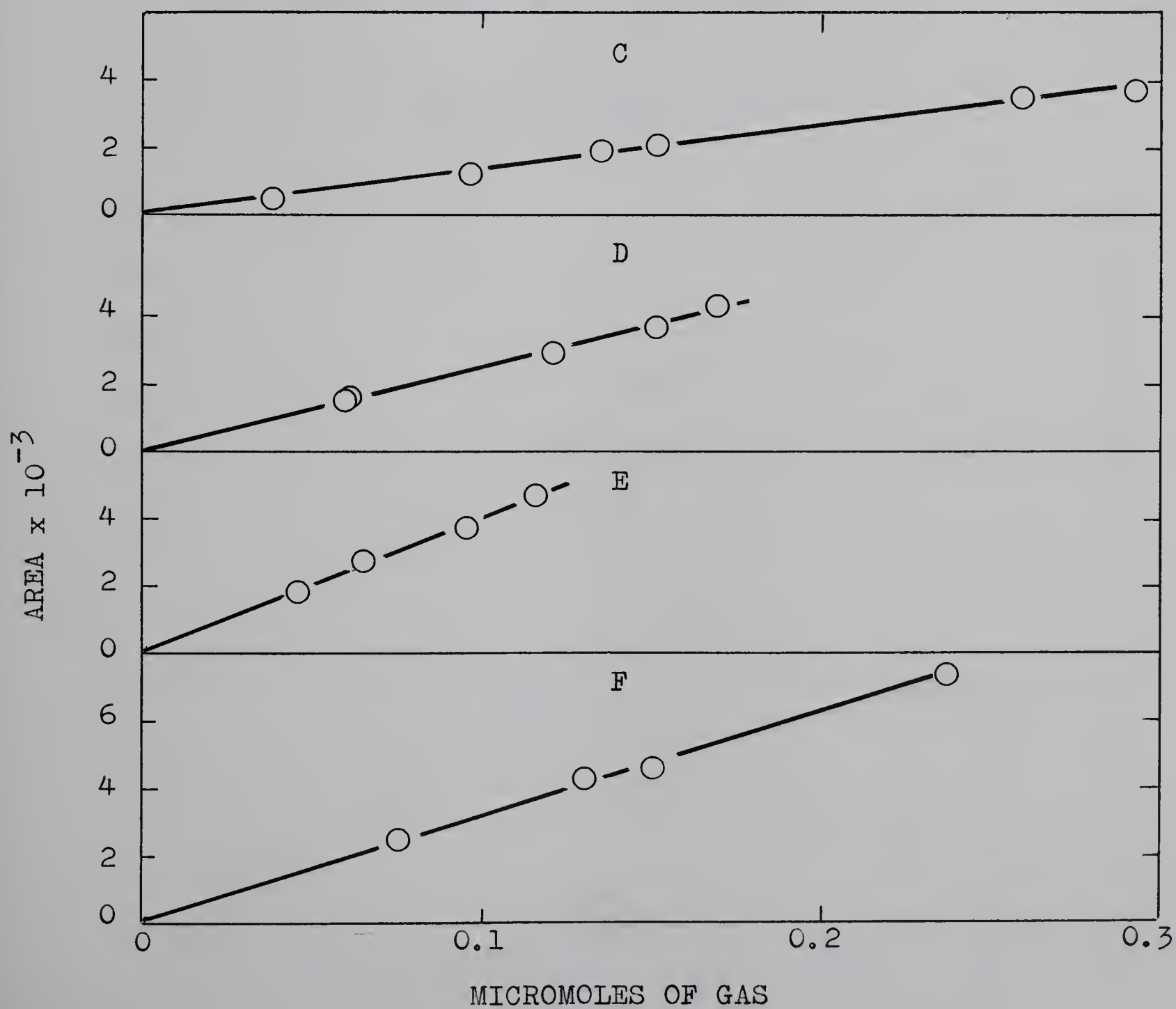
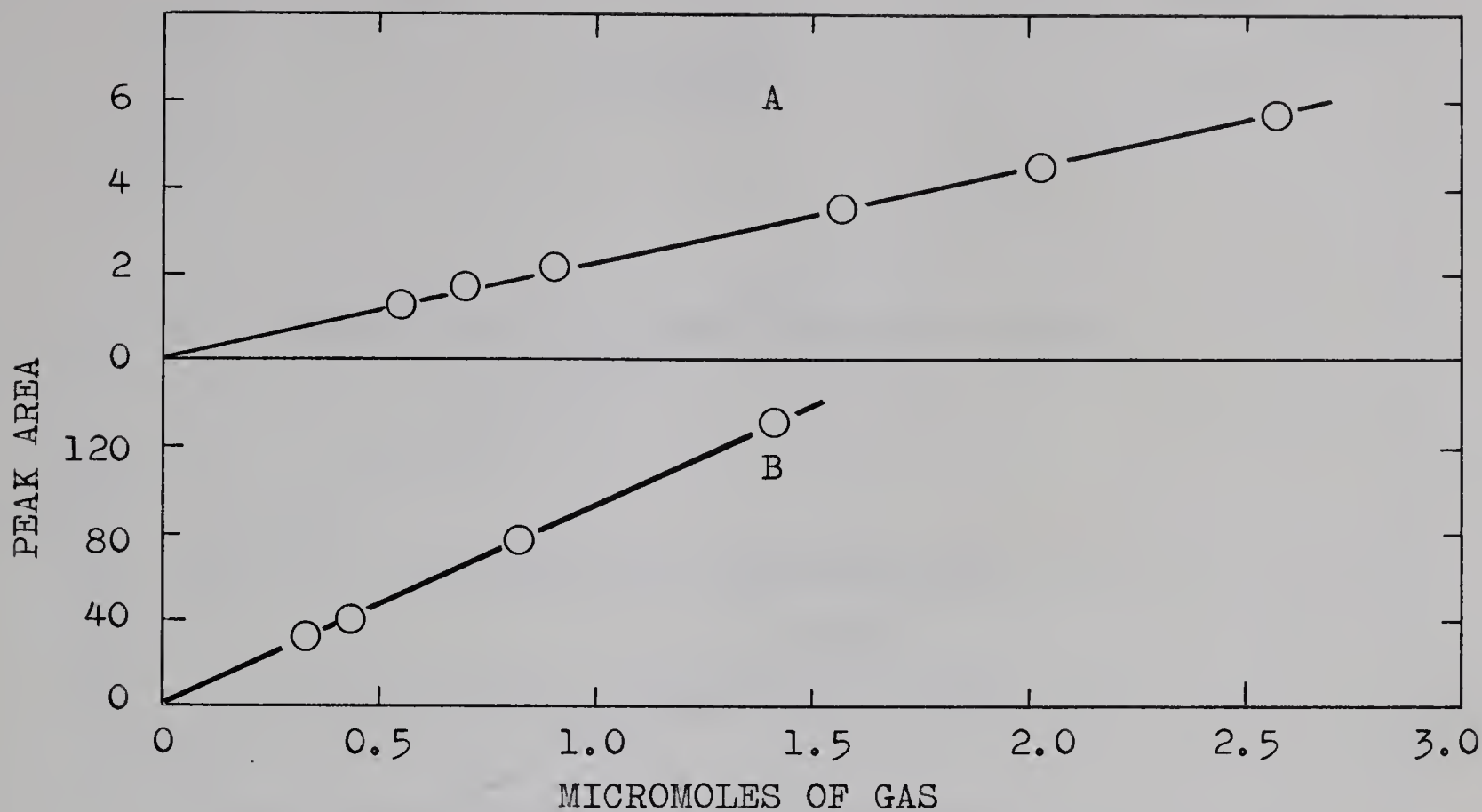


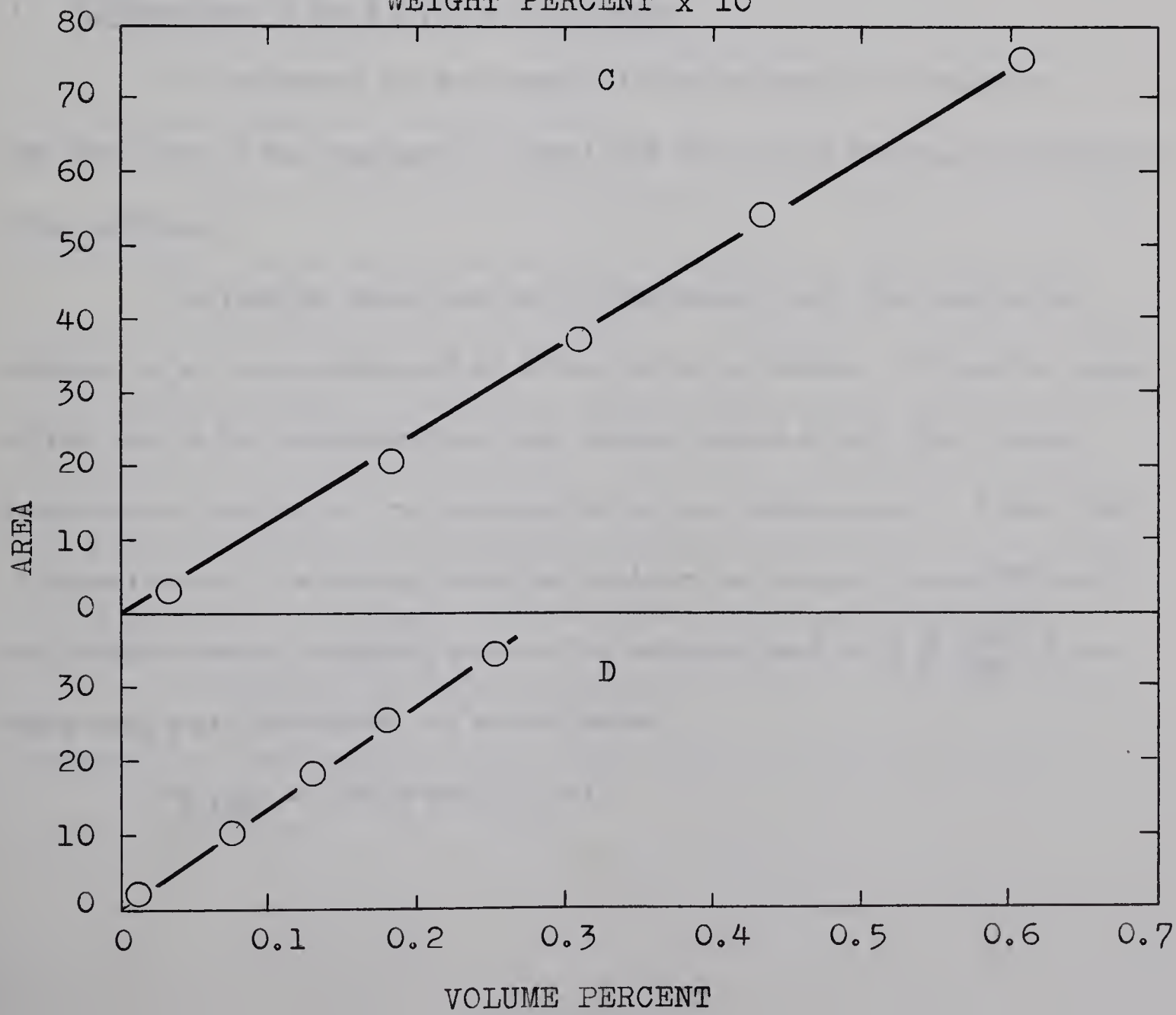
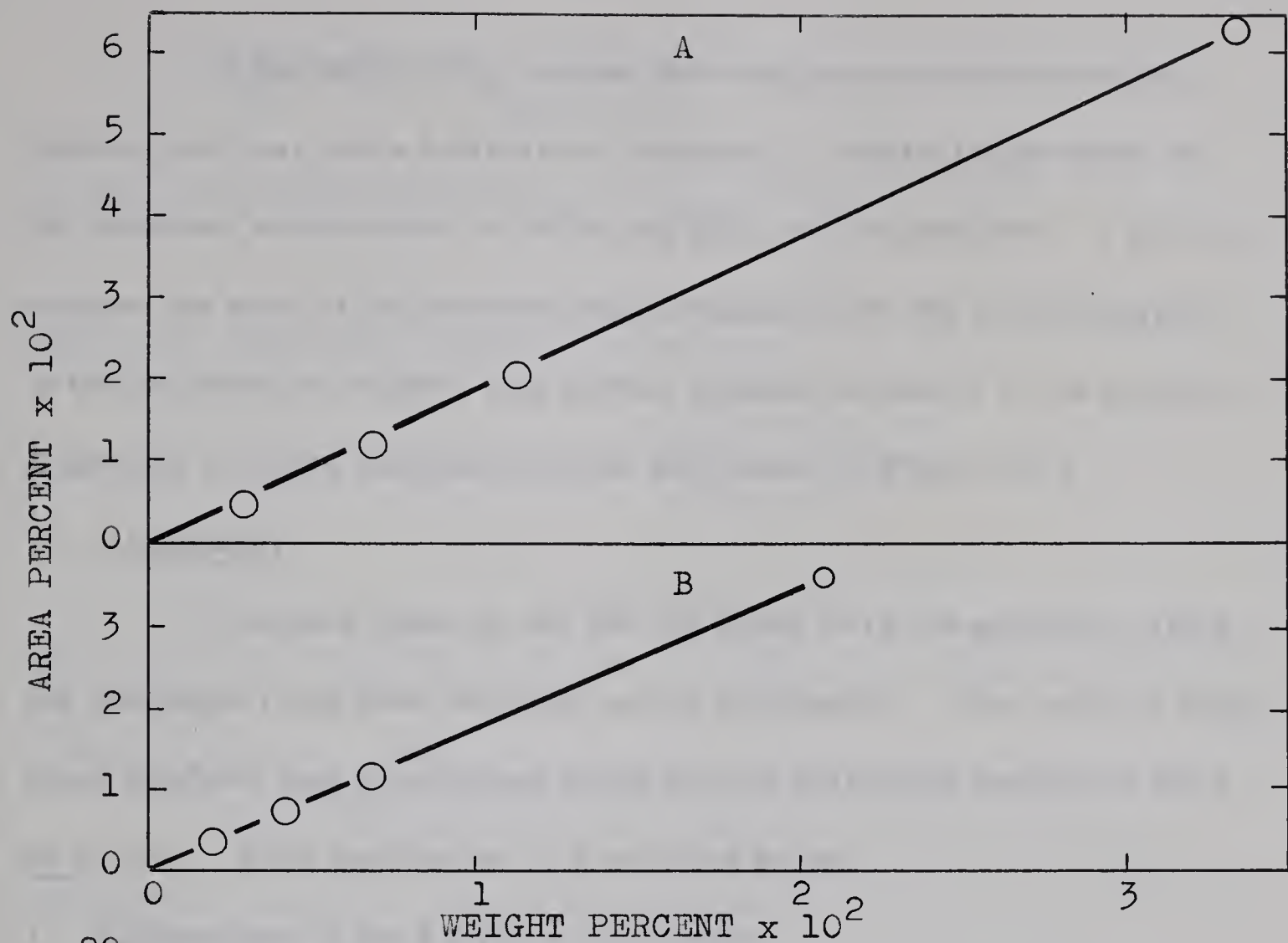
FIGURE II-4Typical Calibration Plots for Liquid Products

A: 1-MC (Hydrogen Flame Detector)

B: n-Tetradecane (Hydrogen Flame Detector)

C: Chloroform (Thermal Conductivity Detector)

D: Hexachloroethane (Thermal Conductivity Detector)







In the MCH-CCl<sub>4</sub> system the area percent versus weight percent plot was not a satisfactory method of calibration because of the different sensitivities of MCH and CCl<sub>4</sub> on the detector. For this system the area of the product peak obtained from the chromatogram of the calibration solution was plotted against volume % of the product. Examples of these calibration plots are shown in Figure II-4.

#### E. Dosimetry

The dose rates in the 500 ml bulbs were measured by using the hydrogen yield from ethylene as the dosimeter. The value of  $G(H_2)$  from ethylene was determined using the ion collection method of Back et al (31). This calibration is described below.

##### 1. Calibration of the Ethylene Dosimeter

To calibrate the dosimeter it was necessary to measure the dose rate in the dosimeter vessel and the rate of hydrogen production from ethylene.

To find the dose rate in the dosimeter cell, the saturation current in air was measured as a function of pressure. From the slope of the plot of the saturation current versus moles of air, the J value (saturation current per micromole) of air was determined. From this J value for air, the energy required to form an ion pair in air (W) and the relative molar stopping powers for ethylene and air ( $\rho_{AIR}^{C_2H_4}$ ) the dose rate was calculated, as shown below.

$$W_{AIR} = 33.8 \text{ ev (35, 36)}$$



$$\rho_{\text{AIR}}^{\text{C}_2\text{H}_4} = 1.17 \text{ (calculated from Bethe's equation (23), see appendix )}$$

$$\text{Dose Rate (ev/mole C}_2\text{H}_4 \text{ sec)} = \frac{J_{\text{AIR}} \times W_{\text{AIR}} \times \rho_{\text{AIR}}^{\text{C}_2\text{H}_4}}{e}$$

where  $e$  = charge on an electron in coulombs

$$\begin{aligned} &= \frac{J_{\text{AIR}} (33.8)(1.17)}{1.602 \times 10^{-19}} \\ &= J_{\text{AIR}} \times 2.46 \times 10^{20} \end{aligned}$$

An example of a saturation current vs moles of air graph is shown in Figure II-5.

Three different cells were used for the measurement of saturation currents. They were all of similar design to that of Back (31) and Armstrong (93, 97). The only difference in the cells was in the material used for the electrodes.

All of the cells were constructed of Pyrex glass in the form of a cylinder, with a central tube down the middle. Ionization cell I (I.C.I.) had stainless steel electrodes. A cylinder of stainless steel foil (0.005") was fitted closely to the wall inside the glass shell of the cell to serve as the outer electrode. The inner electrode consisted of a stainless steel tube (11 mm O.D.) attached to the end wall of the cell by a Kovar seal. A diagram of this cell is shown in Figure II-6.

Ionization cell II (I.C.II) was of all glass construction with the wall, the bottom and the inner glass tube all silvered to form a conducting surface.

FIGURE II-5

Saturation Currents as a Function of Moles of Air

Ionization Cell II

Temperature 30°C

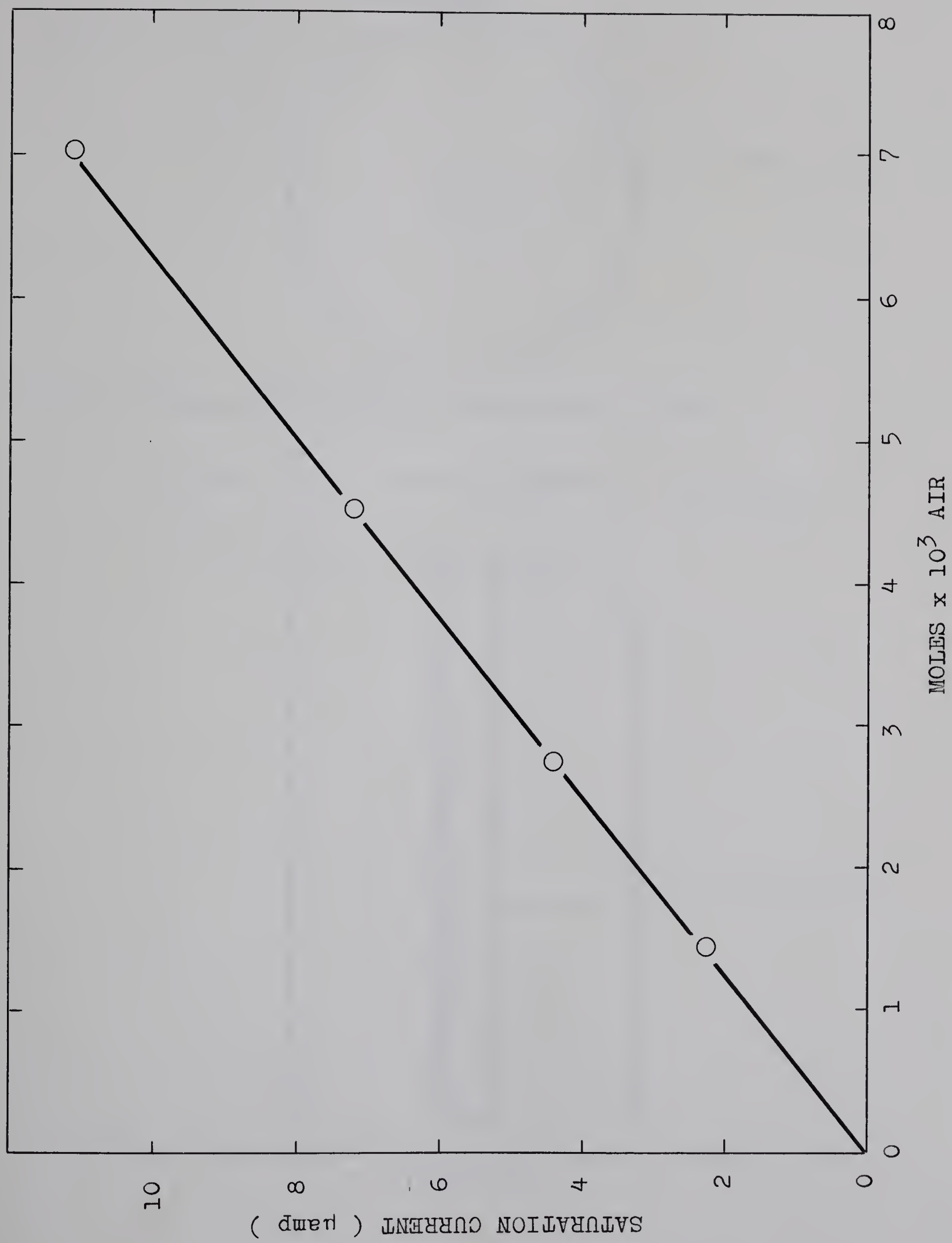
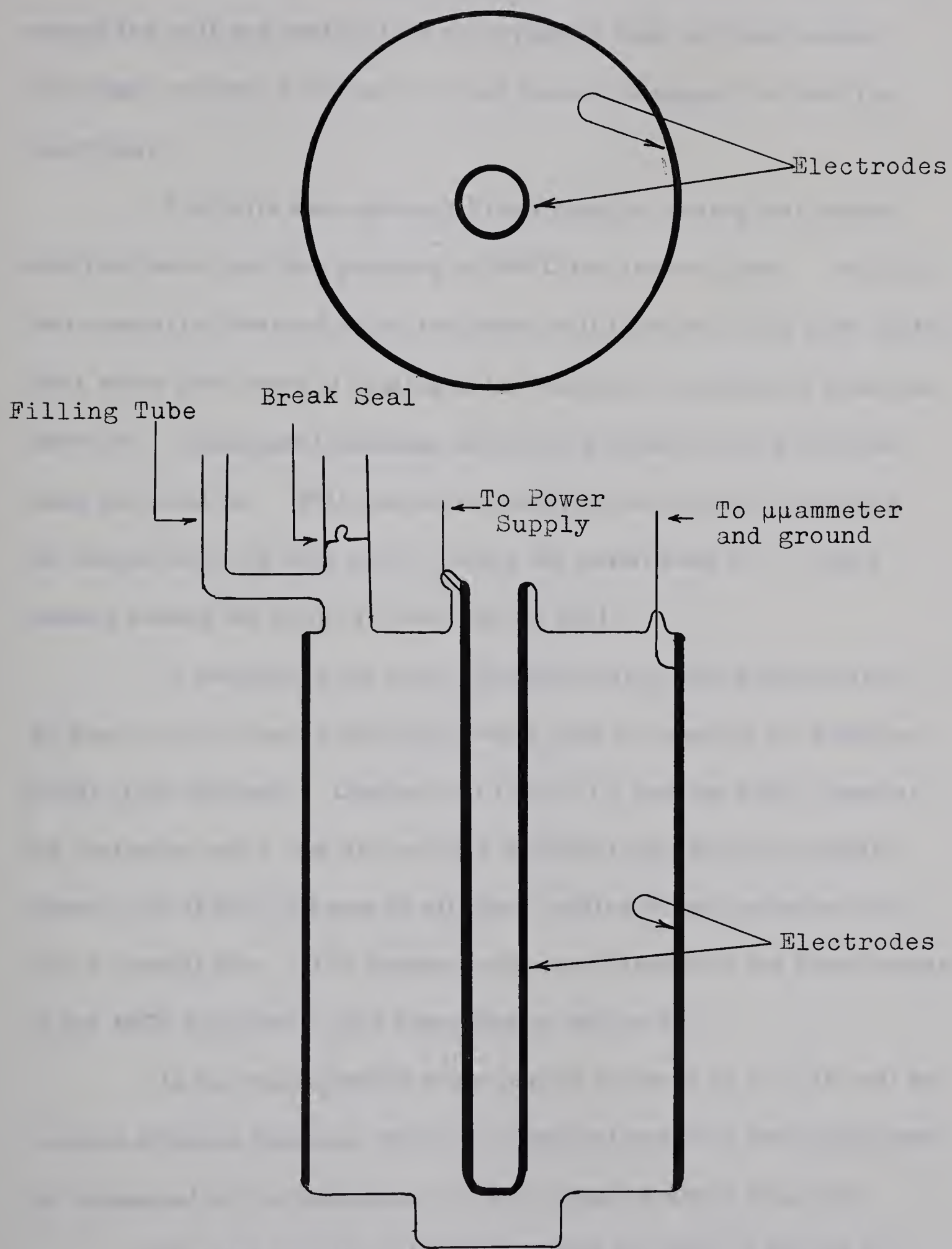




FIGURE II-6Cell for Measurement of Saturation Currents

Scale      0.85 cm      =      1 cm

Volume of Cell = 420 ml





Ionization cell III (I.C.III) was the same as the silvered cell except the wall and central tube were painted with colloidal carbon (Aquadag, Acheson Colloids Co. Port Huron, Michigan) to form the electrodes.

The cells were prepared for filling by rinsing with double distilled water and then pumping at  $450^{\circ}\text{C}$  for several hours. A heavy tarry material distilled out of ionization cell III when it was first heated; after about four hours of heating under vacuum, no additional material came out. Subsequent heatings showed no evidence of this material being distilled out. With ionization cell II it was necessary to bring the temperature up very slowly during the initial bake out. Rapid heating caused the silver to come off the wall.

In addition to the three ionization cells, two dummy cells, i.e. all glass cells without electrodes, were used to measure the hydrogen yields from ethylene. Dummy cell I (D.C.I.) was the same shape as the ionization cells, but did not have a central tube down the middle; dummy cell II (D.C.II) was an all glass replica of the ionization cells with a central tube. The dummy cells were cleaned in the same manner as the MCH radiolysis cells described in section B. 1.

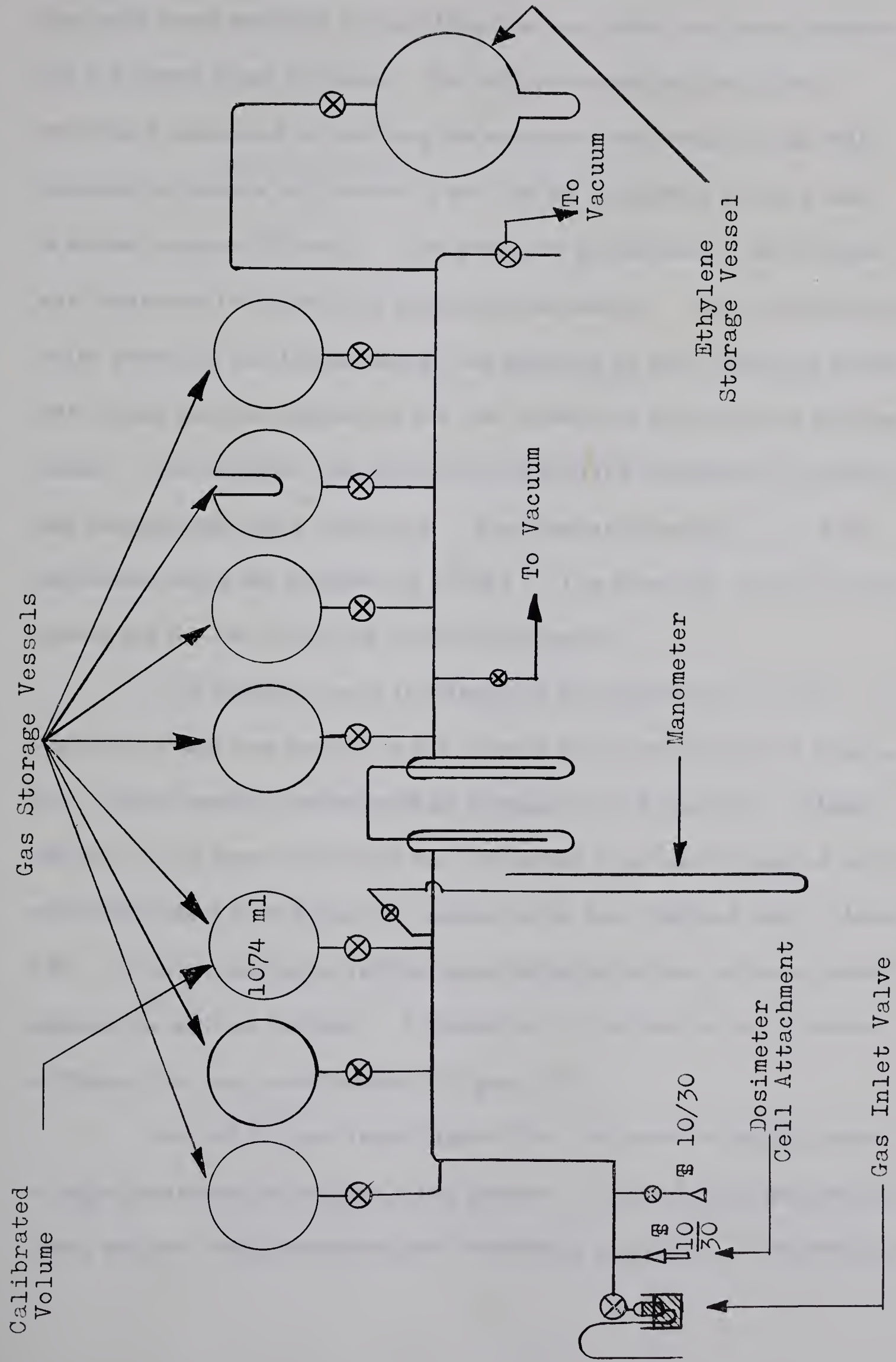
In the measurement of saturation currents in air, as well as in some ethylene samples, where no chemical products were measured, the breakseal on the ionization cell was replaced with a stopcock.

The gas storage and filling system is shown in Figure II-7.

FIGURE II-7

Gas Storage and Dosimeter Filling System







The cells were attached to the filling line and baked out under vacuum for 3-4 hours prior to filling. For ethylene samples the filling procedure consisted of distilling the ethylene from trap to trap while pumping to remove any traces of air, before expanding it into a bulb of known volume (1074 ml). The pressure of ethylene in this volume was measured by means of a mercury manometer. After measurement of the pressure and temperature, the stopcock on the calibrated volume was closed and the ethylene in the line condensed back into the storage vessel. The ethylene was then distilled into the cell and the pressure and temperature were measured. The number of moles was calculated using the relation  $n = PV/RT$ . The stopcock on the cell was closed and the cell removed from the filling line.

The samples were irradiated in the Gammacell at 30°C. A positive voltage was applied to the central electrode of the cell from a D.C. power supply (Spellman High Voltage Co., Bronx N.Y., Model PN-30). The outer electrode was connected to ground through a microammeter (E-H Research Laboratories Inc. Oakland Calif. Model 240). The current observed during irradiation of the cell was plotted against the applied voltage. A typical set of curves for air is shown in Figure II-8 and for ethylene in Figure II-9.

As can be seen from Figure II-8, the current-voltage plots at high pressures do not give a flat plateau. There is a slight positive slope and the slope increases with increasing pressure. The method of

FIGURE II-8Typical Saturation Currents in Air

Temperature 30°

A:  $1.46 \times 10^{-3}$  molesB:  $2.75 \times 10^{-3}$  molesC:  $4.52 \times 10^{-3}$  molesD:  $7.02 \times 10^{-3}$  moles $\Delta$ : Bottom Scale, 1/Voltage

Method of obtaining saturation current from D:

Saturation Current at  $V=0$ ,  $(i_{\text{sat}})_0 = 11.5 \mu\text{amp}$ Saturation Current at  $1/V=0$ ,  $(i_{\text{sat}})_\infty = 10.6 \mu\text{amp}$ Average Saturation Current =  $11.1 \mu\text{amp}$

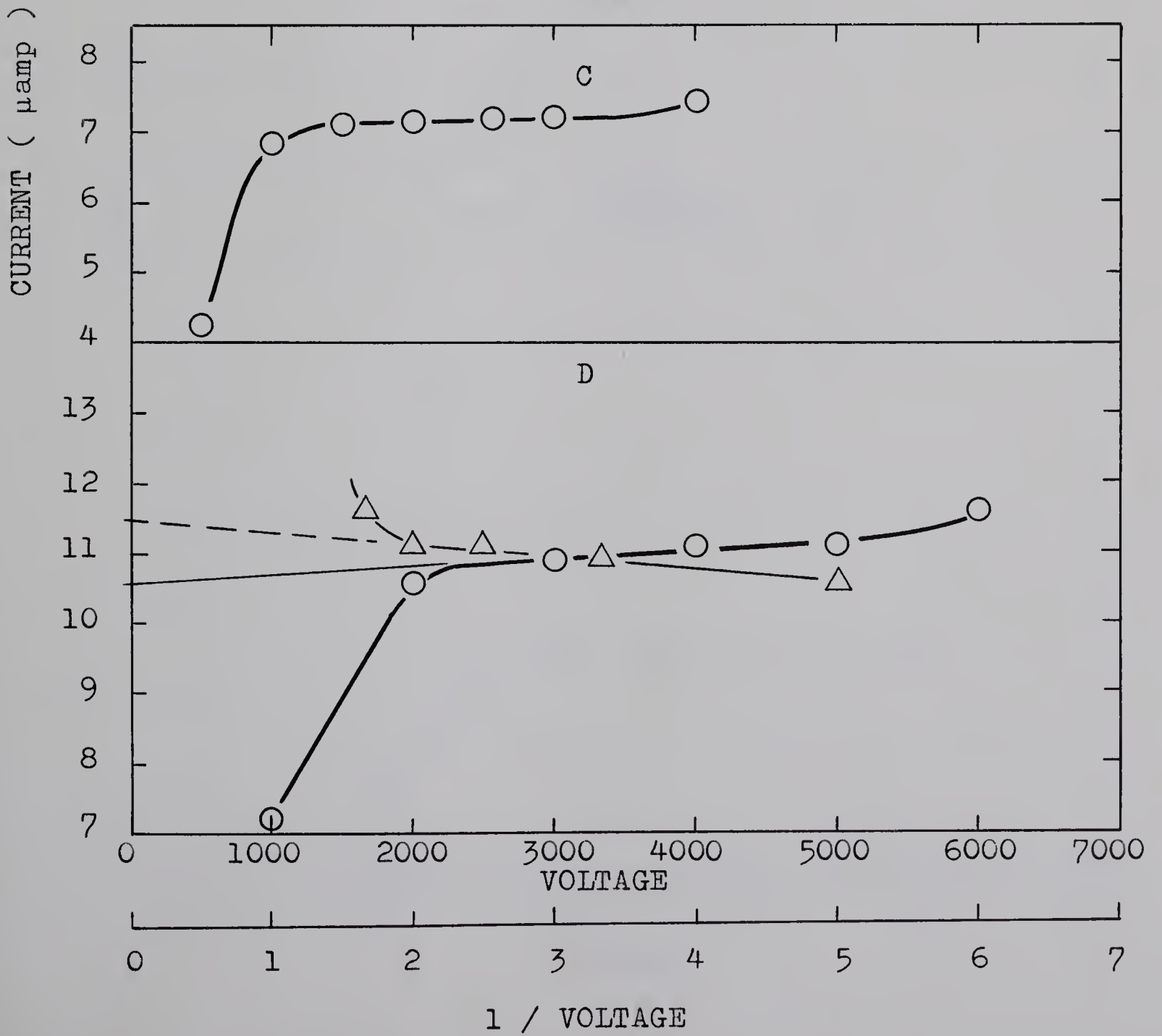
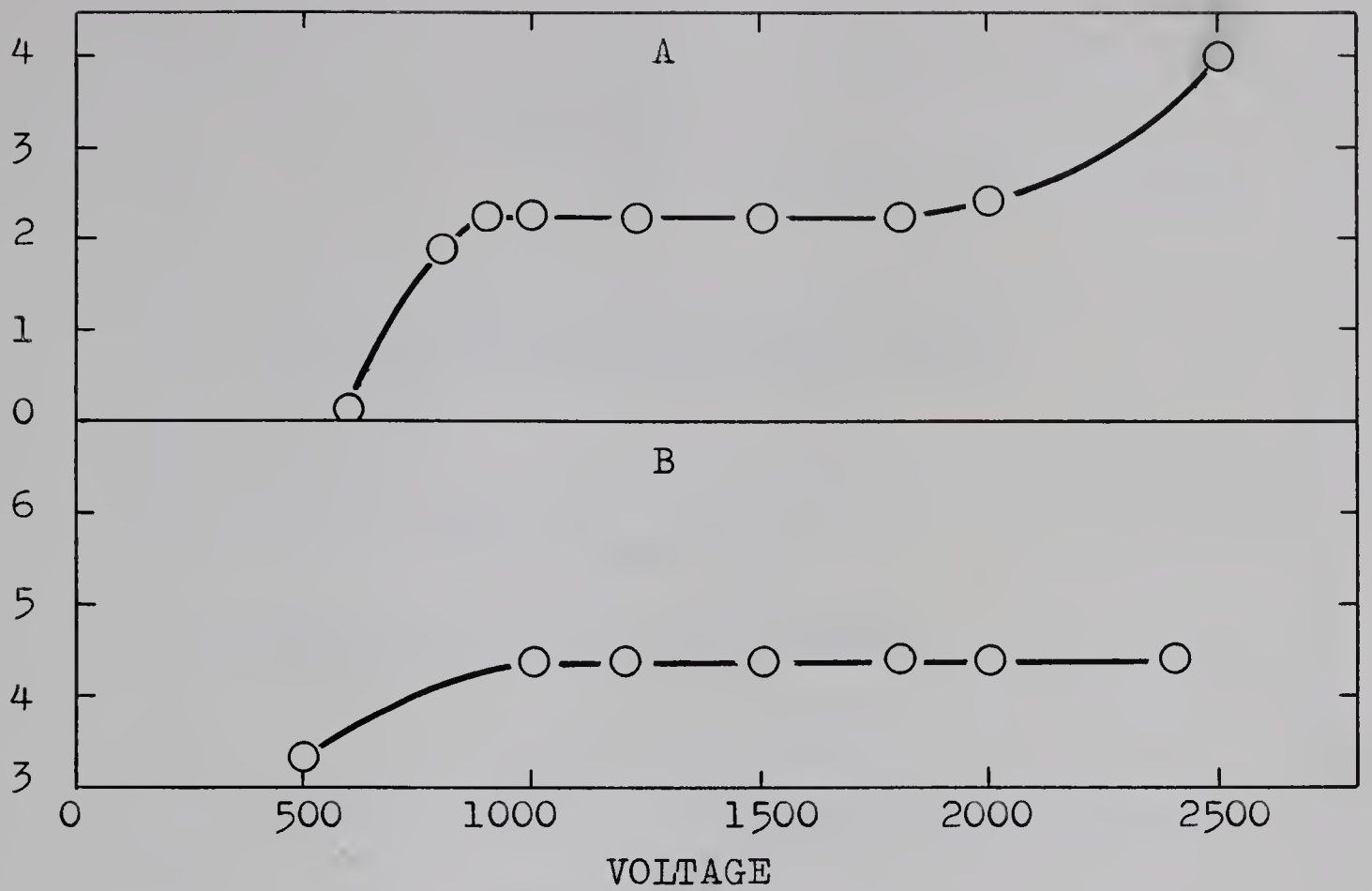


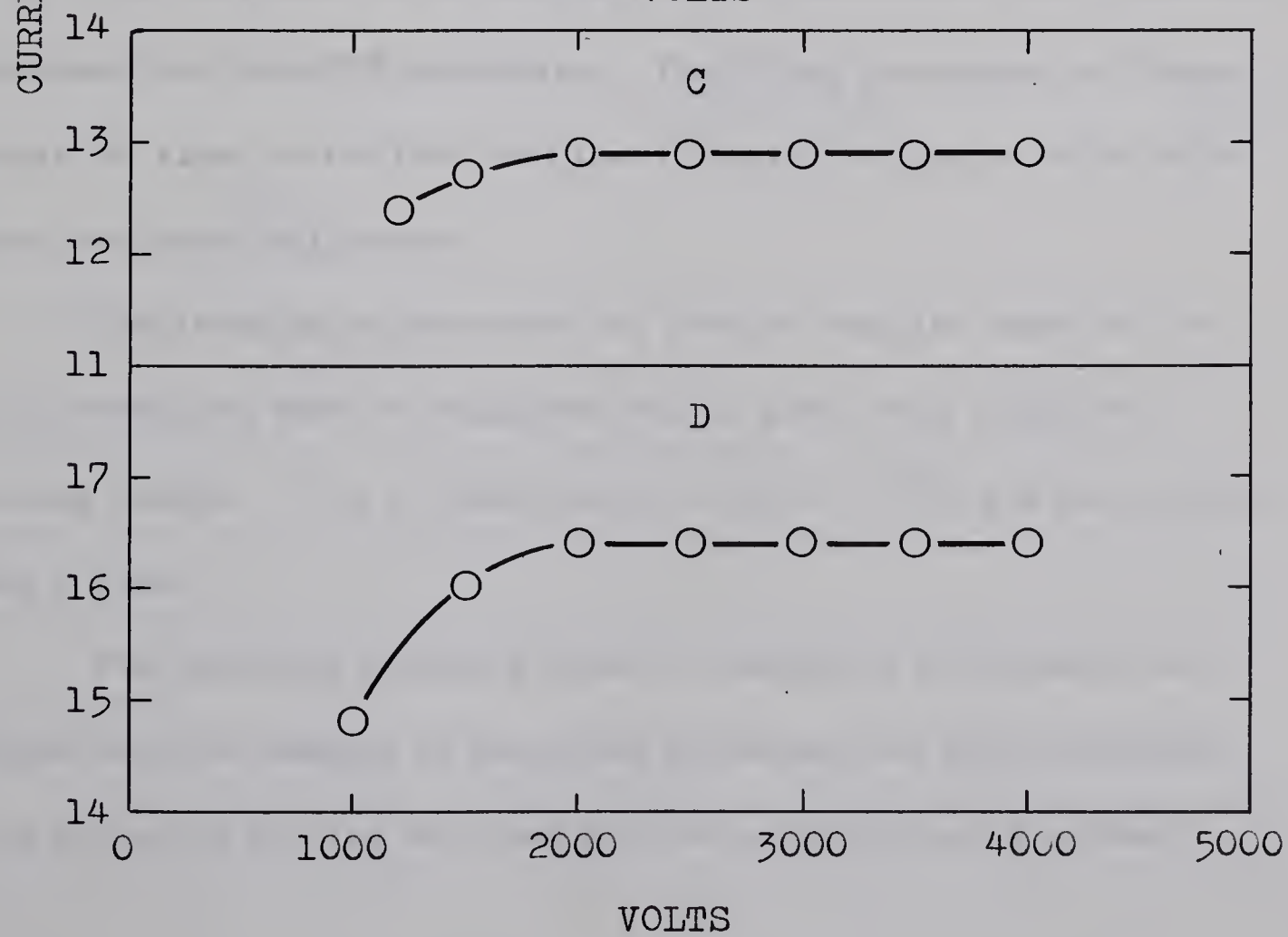
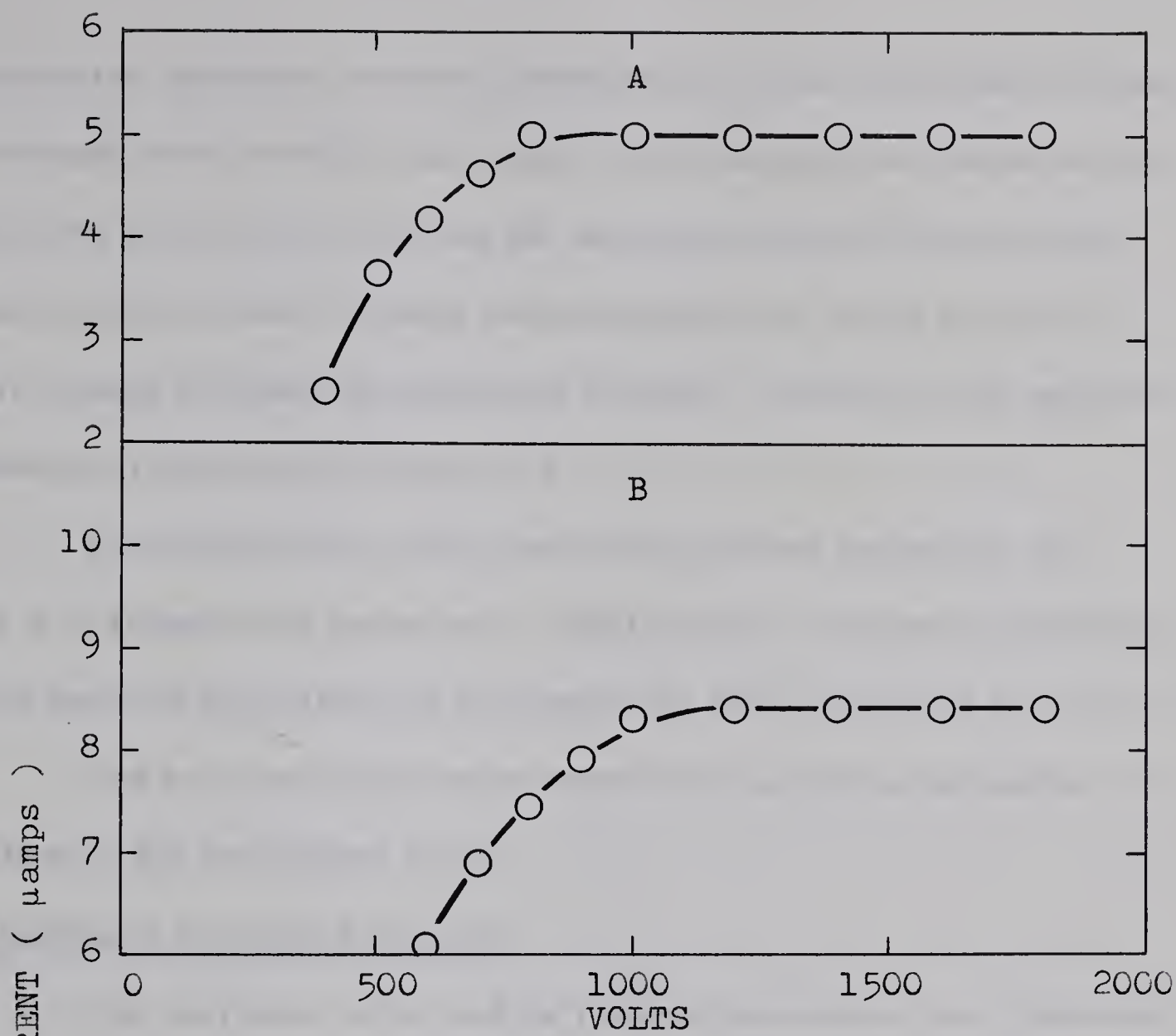


FIGURE II-9Typical Saturation Currents in Ethylene

Temperature 30°

Ionization Cell II (Silver Electrodes )

A: 2.08 x 10<sup>-3</sup> molesB: 3.50 x 10<sup>-3</sup> molesC: 5.40 x 10<sup>-3</sup> molesD: 6.89 x 10<sup>-3</sup> moles





extracting the saturation current from these plots was somewhat arbitrary. The average of two methods was used: (1) extrapolate the linear portion of the curve to zero volts and take the saturation current at zero volts; (2) plot current versus  $1/\text{voltage}$  and extrapolate the linear portion to infinite voltage to obtain the saturation current. These two extrapolation methods are illustrated in Figure II-8.

To complete the calibration of the ethylene dosimeter, the yields of hydrogen were measured. The technique of measuring hydrogen was the same as that described previously for MCH radiolysis (section D.1.).

The hydrogen yields were measured in all three ionization cells, as well as in the two dummy cells.

## 2. Dosimetry for MCH Radiolysis

The dosimeter cells and the cleaning procedure were identical to those used for the MCH radiolysis. The filling procedure for these cells was the same as for that used for filling the ionization cells in the ethylene dosimeter calibration.

The irradiation procedure for ethylene was the same as for the MCH radiolysis with the exception that no power was supplied to the heating mantle. The irradiations were done at  $30^{\circ}\text{C}$  and for varying periods of time.

The hydrogen produced from the radiolysis of ethylene was separated from the sample as described previously for MCH radiolysis with the exception that for most samples the solid nitrogen trap was





replaced by a trap filled with molecular sieve number 5A. (The molecular sieve trap which was used initially, was found to be less convenient than a solid nitrogen trap, hence subsequent experiments were done using solid nitrogen. The same results, within experimental error, were found by both methods.) The molecular sieve trap was immersed in liquid nitrogen in order to hold back the methane and ethylene, allowing the hydrogen to be measured alone in the McLeod gauge. In samples using the solid nitrogen trap, hydrogen and methane were measured by gas chromatography.

The rate of hydrogen production, measured in micromoles per hour per gram of ethylene, was obtained from the slope of the hydrogen yield versus time of radiation plot. The dose rate was calculated as shown below:

$$\text{Dose Rate} = \text{rate of hydrogen production} \left( \frac{\mu\text{moles}}{\text{hr gm C}_2\text{H}_4} \right) \times 6.02 \times 10^{17} \left( \frac{\text{molecules}}{\mu\text{mole}} \right) \\ \times \frac{100}{G(\text{H}_2)}$$

$$\text{where } G(\text{H}_2) = 1.33 \frac{\text{molecules}}{100 \text{ ev}}$$

To convert to dose rate in ev per hour per gram of MCH the dose rate calculated above was multiplied by the ratio of the number of electrons per gram in ethylene to the number of electrons per gram in MCH, which is equal to unity.

(For ethylene and for MCH there are  $0.571N$  electrons per gram, where  $N$  is Avogadro's number.) Therefore the dose rate in  $\text{ev/hr gm C}_2\text{H}_4$



is equal to the dose rate in  $\text{ev/hr gm MCH}$ .

1. Assumptions

2. Calculation of the dose rate

The dose rate is calculated by multiplying the activity of the source by the dose rate constant for the material. The dose rate constant is a function of the material and the geometry of the source.

The dose rate constant for a point source is given by the following equation:

$$D = \frac{A \cdot \Gamma}{r^2}$$

where  $D$  is the dose rate in  $\text{ev/hr gm MCH}$ ,  $A$  is the activity in  $\text{curies}$ ,  $\Gamma$  is the dose rate constant in  $\text{ev/hr gm MCH cm}^2/\text{curie}$ , and  $r$  is the distance from the source in  $\text{cm}$ .

For a distributed source, the dose rate is given by the following equation:

3. Results

4. Discussion

5. Conclusion

6. References

7. Appendix

8. Tables

9. Figures

10. Summary

11. References

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13. Tables

14. Figures

15. Summary

16. References

17. Appendix

18. Tables

19. Figures

20. Summary

21. References

22. Appendix

23. Tables



## RESULTS

A. Dosimetry1. Calibration of Ethylene Dosimeter

The dose rate and yields of hydrogen from ethylene were measured in all three ionization cells. The hydrogen yields were also measured in the two dummy cells.

The J values for air, as measured from the three ionization cells, along with the dose rates calculated from them are stated in Table III-1.

TABLE III-1J-Values and Dose Rates in Air

	I.C.I	I.C.II	I.C.III
	(Steel <u>Electrodes</u> )	(Silver <u>Electrodes</u> )	(Carbon <u>Electrodes</u> )
$J_{\text{Air}}$ (amp/mole)	$1.79 \times 10^{-3}$	$1.75 \times 10^{-3}$	$1.63 \times 10^{-3}$
Dose Rate (ev/hr mole)	$1.59 \times 10^{21}$	$1.55 \times 10^{21}$	$1.45 \times 10^{21}$

Due to the decay of  $^{60}\text{Co}$  with a half life ( $t_{1/2}$ ) of 5.27 years, it was necessary to correct measurements of source intensity to a common reference date. The decay factor is found from the relation  $I/I_0 = e^{-0.1315t}$  where  $I_0$  is the intensity at the reference date, and  $I$  is the intensity after the time  $t$ , in years, has elapsed. These results have





been corrected to January 1, 1965.

The values of  $G(H_2)$  for ethylene in the different ionization cells were calculated using the dose rate measured for that particular cell. For the dummy cells, the average of the dose rates measured in the three ionizations cells were used for calculation of  $G(H_2)$ . The hydrogen yields from the ionization cells were all measured with no voltage applied. These results are tabulated in Table III-2.

The average of the hydrogen yields from all five cells was taken for the calibration of ethylene dosimeter. From Table III-2, the average  $G(H_2)$  is 1.33 with a standard deviation of  $\pm 0.06$ .

Back et al (31) measured the ion pair yield of hydrogen from ethylene to be 0.34 molecules per ion pair. By assuming  $W_{C_2H_4} = 26.5$  ev, they found  $G_{H_2}$  to be 1.28. If the average value of  $W_{C_2H_4}$  as measured from ionization cells I, II & III (25.8 ev) is taken (see Section B.1) Back's value for  $G_{H_2}$  becomes 1.32.

## 2. Dosimetry for MCH Radiolysis

Ethylene was irradiated in 500 ml spherical bulbs, the same as those used for MCH radiolysis, for different lengths of time. The amount of hydrogen formed was measured. These results, corrected for  $^{60}Co$  decay to January 1, 1965, are shown in Figure III-1. From the slope of line in Figure III-1, the rate of production of hydrogen is 1.13 moles per hour per gram of ethylene.

The dose rate in the MCH radiolysis cells was then calculated



TABLE III-2Hydrogen Yields from Ethylene Radiolysis

<u>Cell</u>	<u>Dose (ev/g)</u>	<u>Pressure (Torr)</u>	<u>G<sub>(H<sub>2</sub>)</sub></u>
Dummy Cell I	5.36 x 10 <sup>19</sup>	282	1.30
Dummy Cell I	10.8 x 10 <sup>19</sup>	286	1.32
Dummy Cell II	9.87 x 10 <sup>19</sup>	278	1.24
Dummy Cell II	9.87 x 10 <sup>19</sup>	266	1.28
Ionization Cell I (Steel electrodes)	10.3 x 10 <sup>19</sup>	283	1.44
Ionization Cell I (Steel electrodes)	10.3 x 10 <sup>19</sup>	284	1.41
Ionization Cell II (Silver electrodes)	4.93 x 10 <sup>19</sup>	281	1.36
Ionization Cell II (Silver electrodes)	9.87 x 10 <sup>19</sup>	297	1.33
Ionization Cell III (Carbon electrodes)	4.61 x 10 <sup>19</sup>	277	1.26
Ionization Cell III (Carbon electrodes)	9.20 x 10 <sup>19</sup>	283	1.35

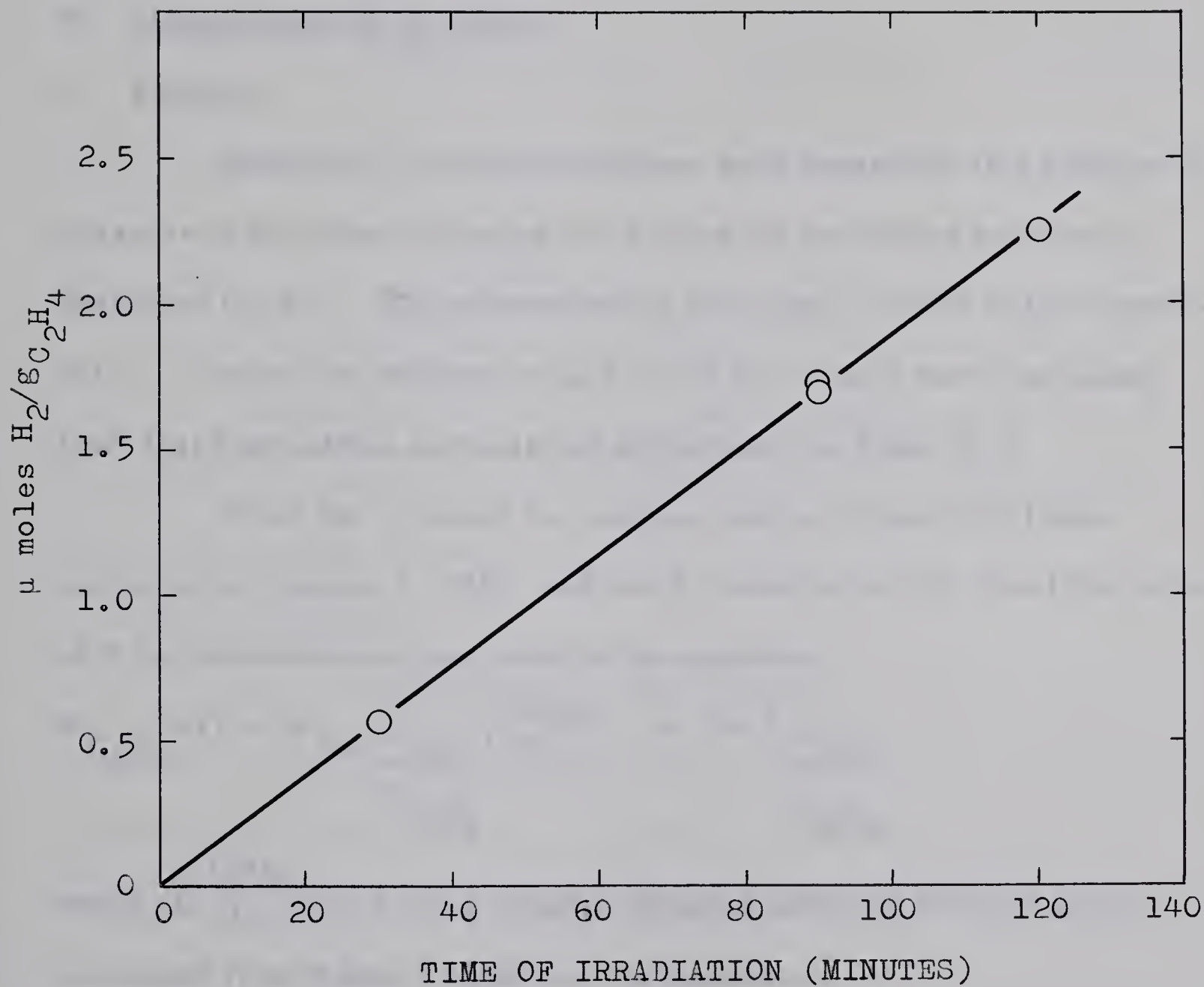
Ave. 1.33 ± 0.06

FIGURE III-1

Hydrogen Production from Ethylene in Gammacell

January 1 , 1965







as shown below.

$$\begin{aligned} \text{Dose Rate} &= 1.13 \frac{\mu\text{moles}}{\text{hr g C}_2\text{H}_4} \times 6.02 \times 10^{17} \frac{\text{molecules}}{\mu\text{mole}} \times \frac{100 \text{ ev}}{1.33 \text{ molecules}} \\ &= 5.12 \times 10^{19} \text{ ev/hr g C}_2\text{H}_4 = 5.12 \times 10^{19} \text{ ev/hr g MCH} \end{aligned}$$

## B. Measurement of W-Value

### 1. Ethylene

Saturation currents in ethylene were measured as a function of pressure in the three ionization cells using the procedure previously described for air. The measurements were done at 30°C in the Gamma-cell. J-values for ethylene in each of the three cells were calculated from these saturation currents and are present in Table III-3.

From the J-values for ethylene and air (Table III-1) both corrected to January 1, 1965, and the W-value for air (33.8 ev) the value of W for ethylene was calculated by the equation:

$$W_{\text{C}_2\text{H}_4} (\text{eV}) = W_{\text{Air}} \frac{J_{\text{Air}}}{J_{\text{C}_2\text{H}_4}} \rho_{\text{Air}}^{\text{C}_2\text{H}_4} = 39.5 \frac{J_{\text{Air}}}{J_{\text{C}_2\text{H}_4}}$$

where  $\rho_{\text{Air}}^{\text{C}_2\text{H}_4} = 1.17$ , the relative stopping power of ethylene and air calculated from Bethe's equation, see Appendix.

The W-values for ethylene, calculated from the above equation, as measured in the three ionization cells with different electrode materials are tabulated in Table III-3.



TABLE III-3

J-Values and W-Values for Ethylene, 30°C

	I.C.I	I.C.II	I.C.III
	(Stainless Steel Electrodes)	(Silver Electrodes)	(Carbon Electrodes)
$J_{C_2H_4}$ (amp/mole)	$2.82 \times 10^{-3}$	$2.65 \times 10^{-3}$	$2.47 \times 10^{-3}$
$W_{C_2H_4}$ (ev)	25.1	26.1	26.1

The average value for  $W_{C_2H_4}$  from these three cells is 25.8 eV. This value is in good agreement with the values of 25.9 eV obtained by Whyte (96) and Meisels (32).

## 2. Methylcyclohexane

Since this project was concerned with the radiolysis of methylcyclohexane vapor, it was desirable to know the average energy required to form an ion pair in this material under radiolysis conditions. To obtain the W-value of MCH vapor at 110°C, saturation currents were measured in ionization cell II (silver electrodes) with varying amounts of MCH. The only change required in the experimental procedure from that used for air and ethylene was the enclosure of the cell in a heating jacket to allow heating of the cell. Good plateaus were obtained on the current-voltage plots for MCH vapor (See Figure III-2). Saturation



FIGURE III-2

Saturation Currents in MCH at 110<sup>o</sup> C

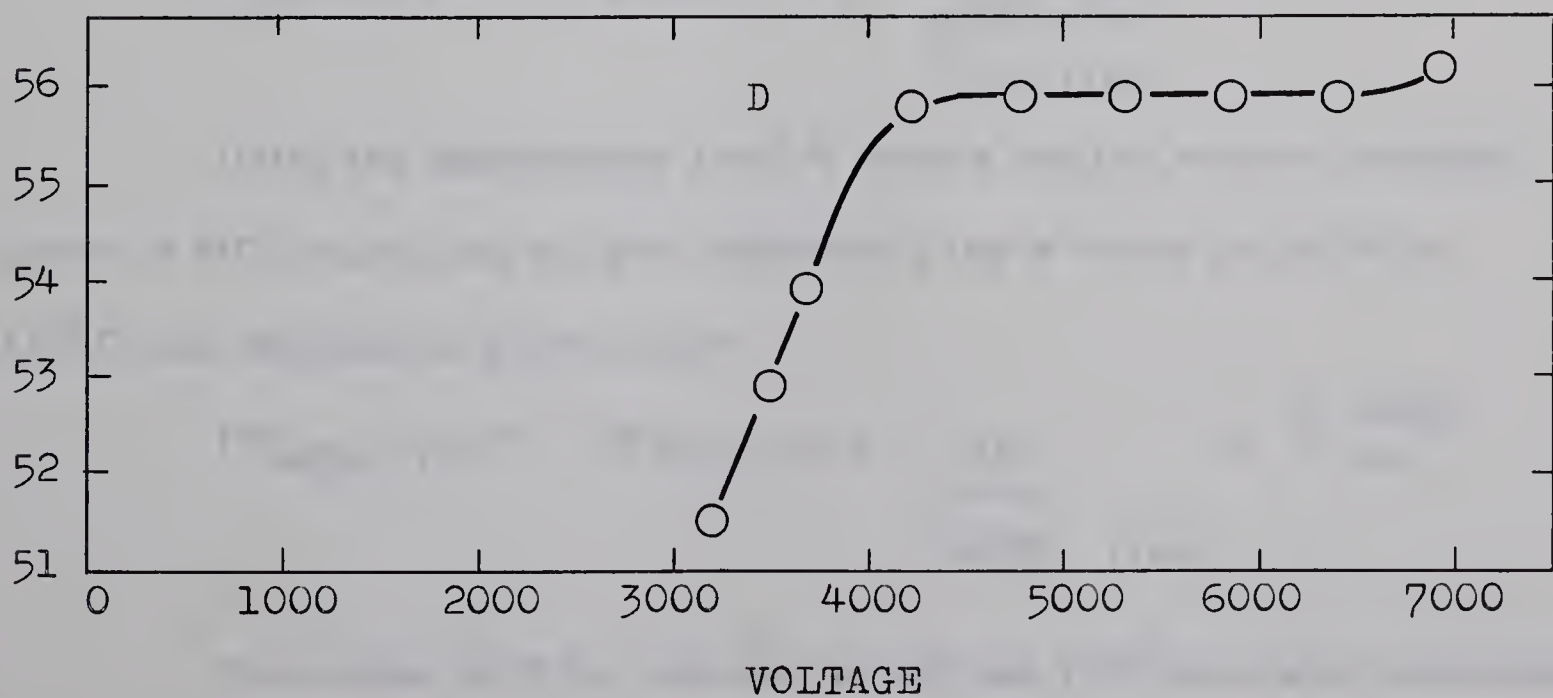
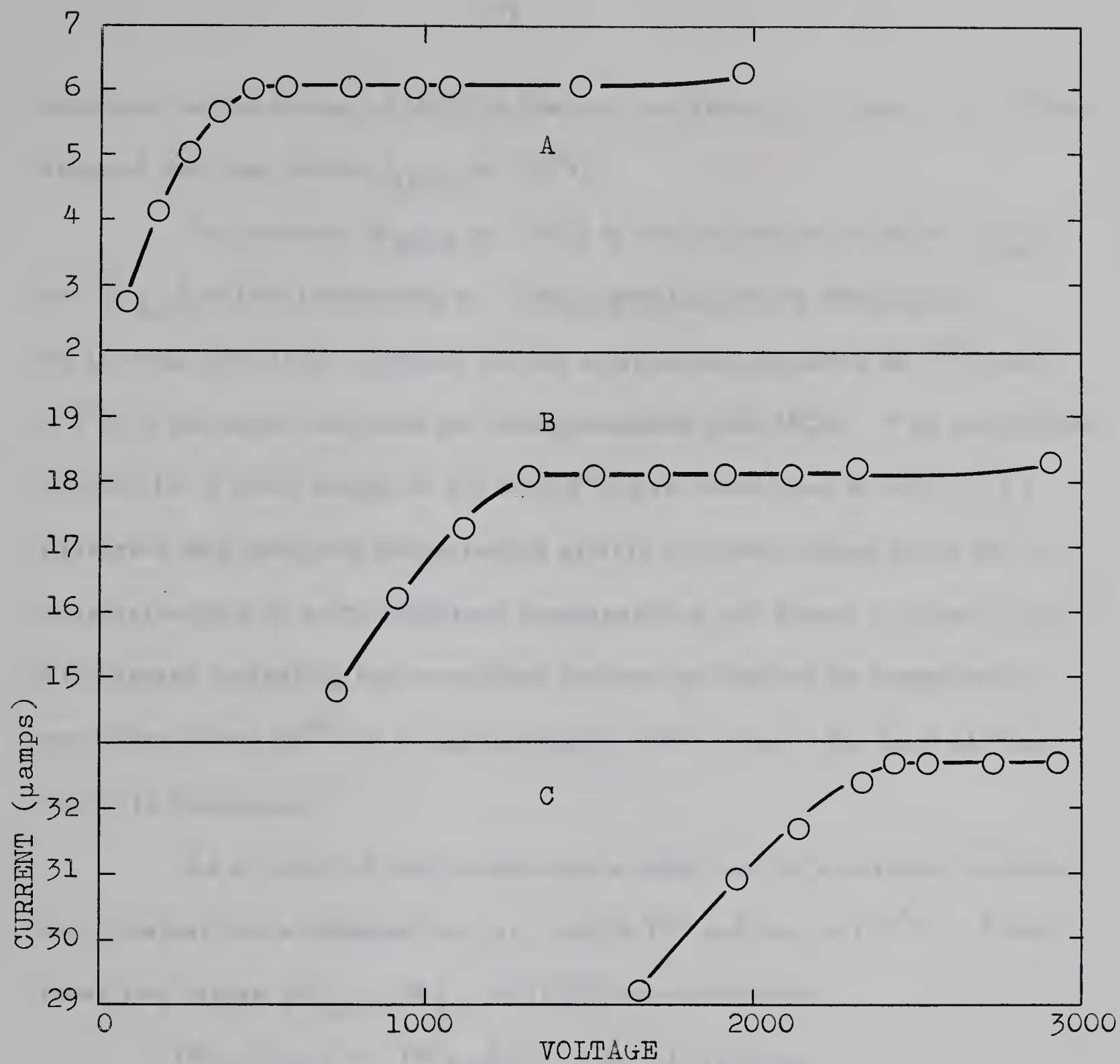
(Ionization Cell II    May 4, 1966)

A:     $0.72 \times 10^{-3}$  moles

B:     $2.19 \times 10^{-3}$  moles

C:     $4.06 \times 10^{-3}$  moles

D:     $7.03 \times 10^{-3}$  moles





currents versus moles of MCH in the cell are shown in Figure III-3. The slope of this line yields  $J_{\text{MCH}}$  at  $110^{\circ}\text{C}$ .

To calculate  $W_{\text{MCH}}$  at  $110^{\circ}\text{C}$  it was necessary to know  $(J_{\text{Air}})$  and  $(W_{\text{Air}})$  at this temperature. These numbers were obtained by measuring saturation currents for air at several pressures at  $30^{\circ}\text{C}$  and  $110^{\circ}\text{C}$  in the same cell used for measurements with MCH. The saturation current for a fixed weight of air at  $110^{\circ}\text{C}$  was lower than at  $30^{\circ}\text{C}$ . To illustrate this observed temperature effect, current-voltage plots for a constant weight of air at different temperatures are shown in Figure III-4. The plateau indicating the saturation current is lowered by temperature increases above  $60^{\circ}\text{C}$  up to approximately  $150^{\circ}\text{C}$  where the good plateau starts to disappear.

As a result of this temperature effect on the saturation current two J-values were obtained for air, one at  $30^{\circ}$  and one at  $110^{\circ}\text{C}$ . From these two values of  $J_{\text{Air}}$ ,  $W_{\text{Air}}$  at  $110^{\circ}\text{C}$  was calculated.

$$(W_{\text{Air}})_{110^{\circ}} = (W_{\text{Air}})_{30^{\circ}} \times \frac{(J_{\text{Air}})_{30^{\circ}}}{(J_{\text{Air}})_{110^{\circ}}}$$

Using the appropriate J and W values and the relative stopping power of MCH vapor and air (see Appendix .) the W-value for MCH at  $110^{\circ}\text{C}$  was obtained as shown below.

$$(W_{\text{MCH}})_{110^{\circ}} = (W_{\text{Air}})_{110^{\circ}} \times \frac{J_{\text{Air}}}{J_{\text{MCH}} \text{ } 110^{\circ}} \times \rho_{\text{Air}}^{\text{MCH}}$$

The values of W for ethylene at  $30^{\circ}$  and  $110^{\circ}$  were also measured.

FIGURE III-3

Saturation Currents at 110°C as a Function of Moles of MCH



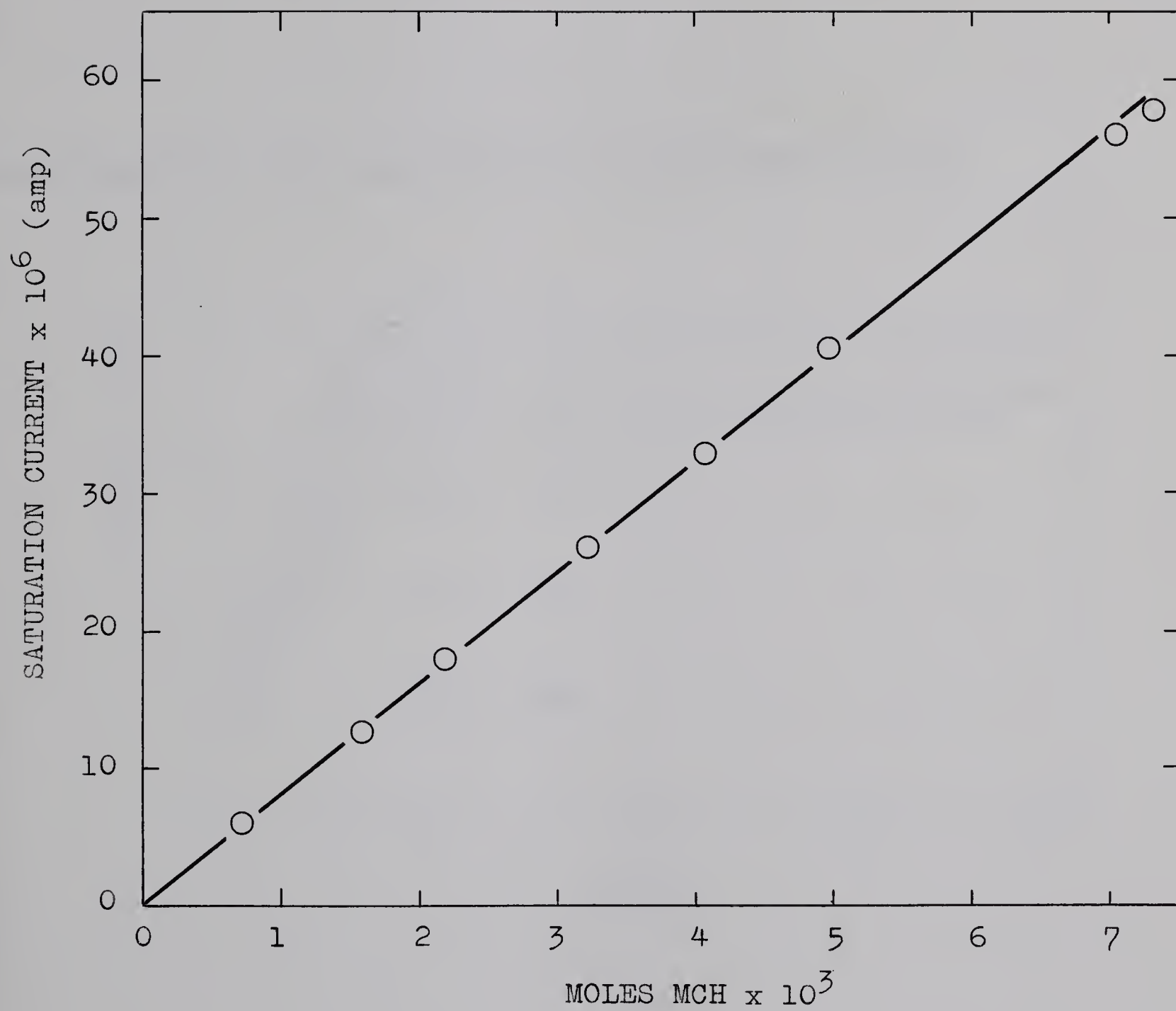


FIGURE III-4

Current-Voltage Plots for Air Measured at Different Temperatures

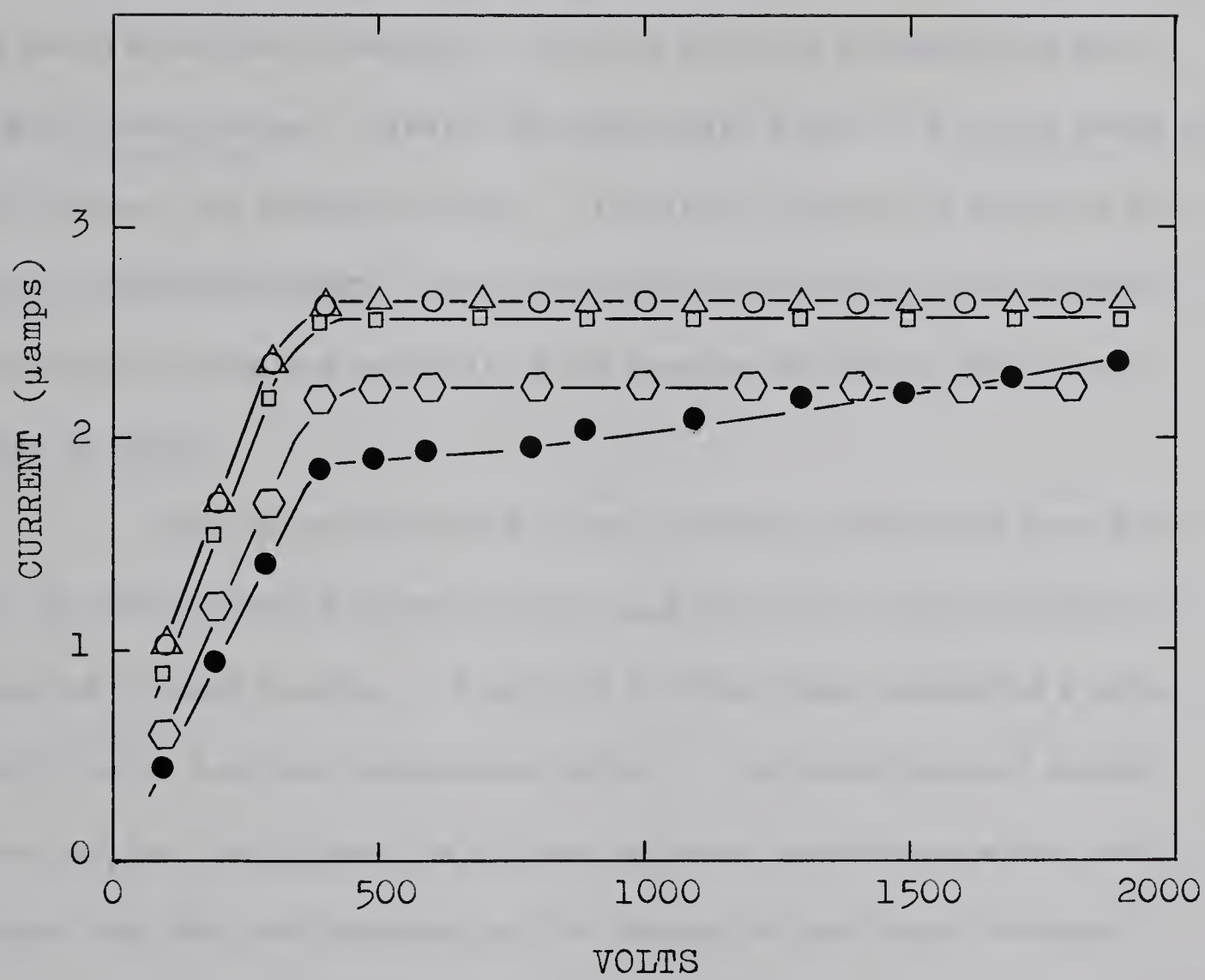
○: 25°C

△: 57°C

□: 77°C

⬡: 110°C

●: 150°C





The results of these experiments are summarized in Table III-4.

C. Radiolysis of Methylcyclohexane Vapor

In the early stages of this project, the yield of hydrogen from MCH vapor was not reproducible from one period of time to another. The hydrogen yield remained constant at a fixed seemingly reproducible value for several series of samples, and then abruptly changed to a new (higher) fixed value. Several attempts were made to find the cause of this change, but without success. Different methods of cleaning the cells, different methods of purifying the starting material, different methods of filling and analysis of the sample all had no effect on the value of  $G(H_2)$ .

The values presented in the previous section for pure MCH are the most recent determinations, and have been reproducible over a period of eight months. The yield of total dimer exhibited a somewhat similar but less pronounced effect. The experimental scatter observed for this product in a given series of experiments was much larger than that for hydrogen so the change of yield was contained within the scatter. The yields of the other products were reproducible within experimental error throughout the project.

1. Effect of Dose

The irradiations were done in the Gammacell. The samples contained 0.78 gm of MCH and were irradiated at  $110 \pm 5^\circ C$ . The total extent of decomposition of the MCH at the highest dose used was 0.1 percent.





TABLE III-4J- and W-Values for Air, MCH, and C<sub>2</sub>H<sub>4</sub> at 30° and 110°C

<u>Temperature</u>	<u>30°C</u>	<u>110°C</u>
J <sub>Air</sub> (Amp/Mole)	1.32 x 10 <sup>-3</sup>	1.24 x 10 <sup>-3</sup>
J <sub>MCH</sub> (Amp/Mole)	-	8.08 x 10 <sup>-3</sup>
J <sub>C<sub>2</sub>H<sub>4</sub></sub> (Amp/Mole)	2.01 x 10 <sup>-3</sup>	1.87 x 10 <sup>-3</sup>
W <sub>Air</sub> (eV)	33.8	36.0
W <sub>C<sub>2</sub>H<sub>4</sub></sub> (eV)	26.1	27.9
W <sub>MCH</sub> (eV)	-	22.6



### a. Gaseous Products

The main gaseous products resulting from the radiolysis of MCH are hydrogen, methane, ethylene, and propylene. Other gaseous products, in small amounts, include ethane, propane, acetylene, various isomers of the butenes and normal butane. The normal butane may also include some isobutane. The butenes consisted of two peaks, the first of which was butene-1, the second was a multiple peak consisting of butene-2 and isobutylene.

The yields of these gaseous products, with the exception of the butenes, as a function of dose, are shown in Figures III-5, III-6, and III-7, and are tabulated in Table III-5.

The  $C_4$  products were measured with much uncertainty. Because of their solubility in MCH, they could not be completely separated from the liquid, during the  $-112^{\circ}\text{C}$  distillation. From analysis of the liquid remaining after the  $-112^{\circ}\text{C}$  fraction had been removed, it was estimated that less than 40% of the n-butane was removed as a gas. The yields of n-butane in Figure III-7 represent the amount measured as a gas plus that estimated in the liquid. The amount of the butenes that were in the liquid could not be measured because the  $C_5$  liquid products interfered on the silica gel column. For this reason, meaningful yields of the butenes could not be determined.

### b. Liquid Products

The liquid products resulting from the radiolysis of MCH vapor

FIGURE III-5

Yields of Hydrogen and Methane as a Function of Dose

○: Hydrogen

△: Methane



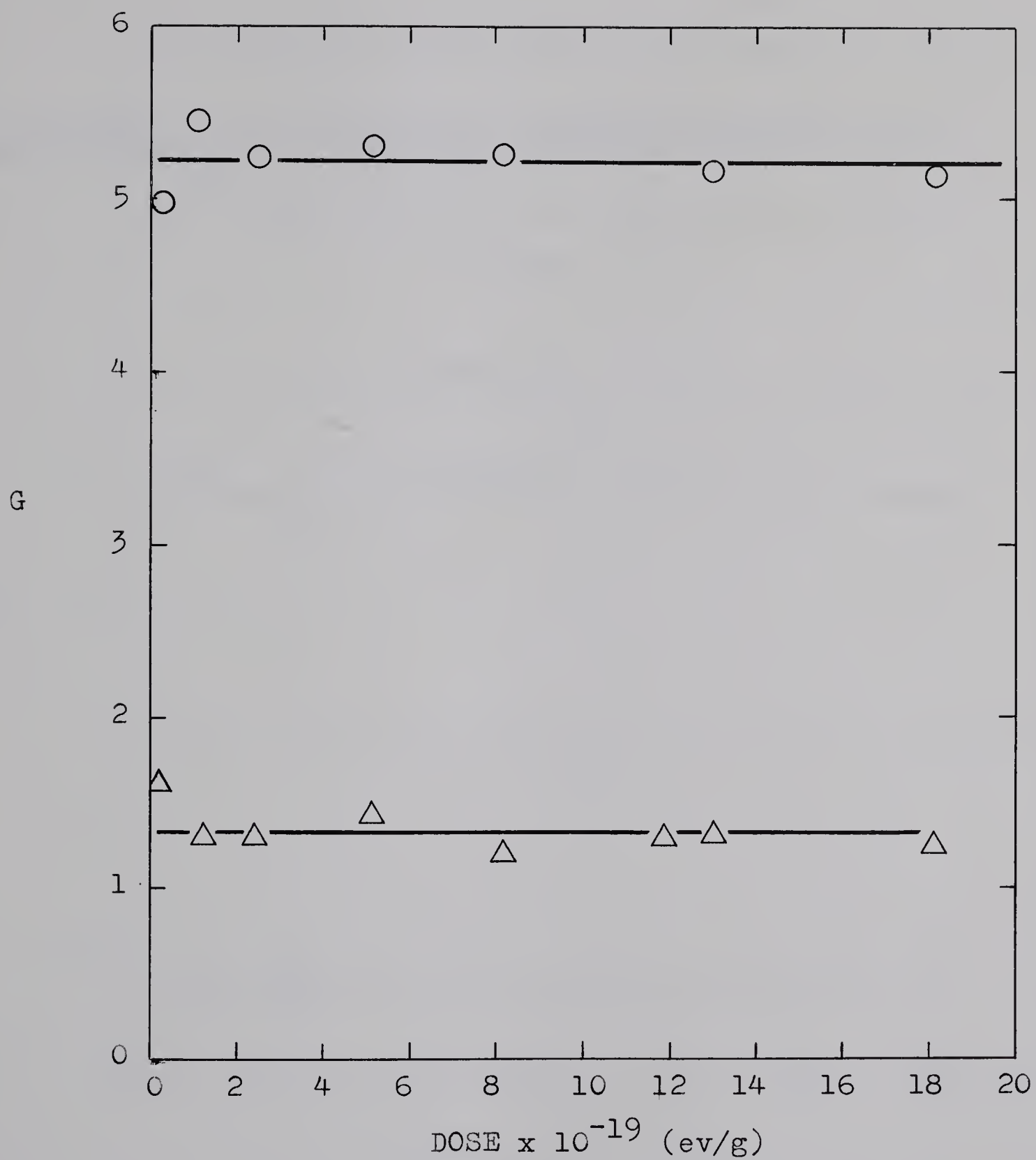


FIGURE III-6

Yields of Ethylene , Propylene , and Acetylene as a Function of Dose

A:     Ethylene

B:     Propylene

C:     Acetylene

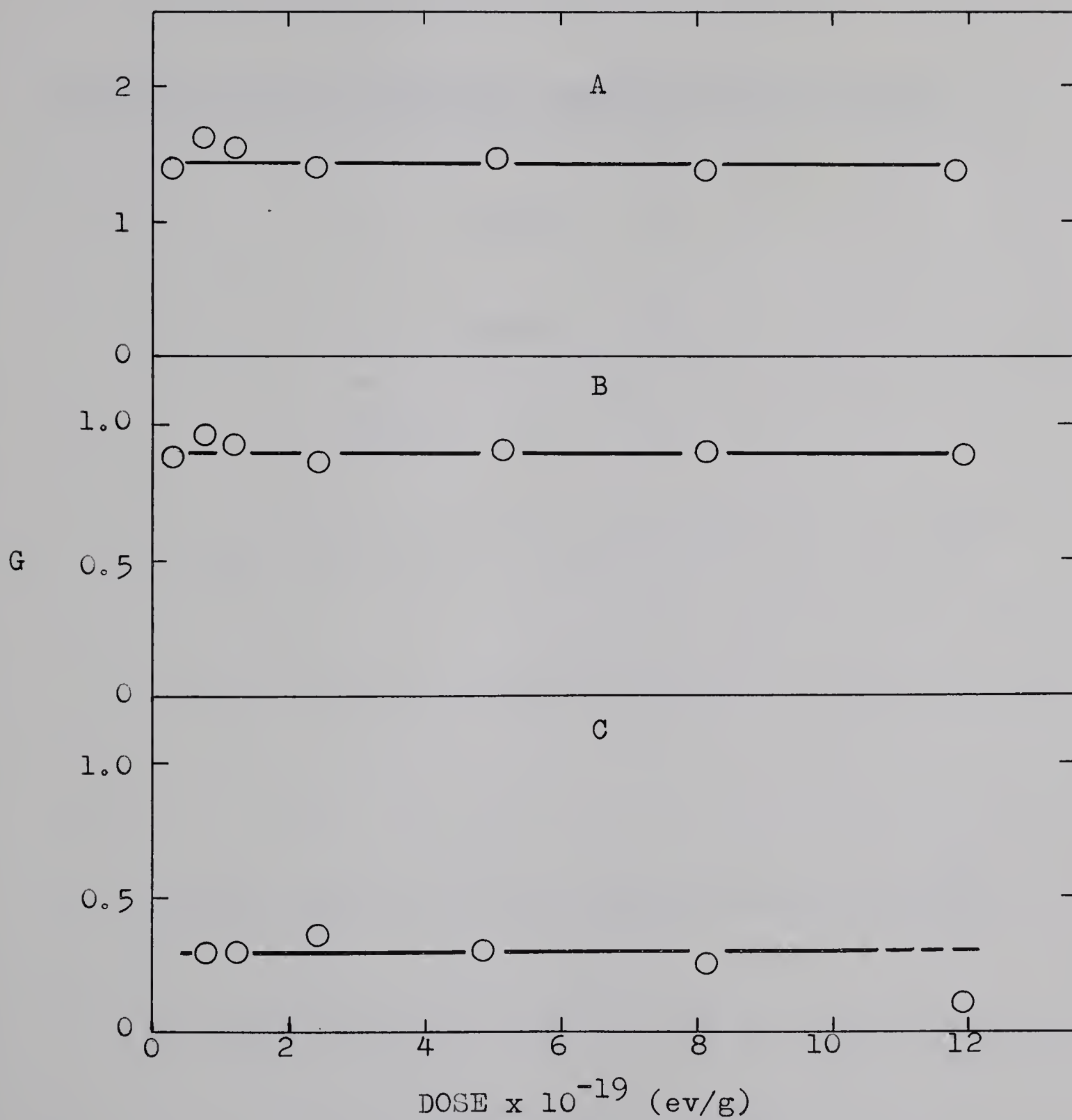


FIGURE III-7

Yields of Ethane , Propane , and Butane as a Function of Dose

A: Ethane

B: Propane

C: n- + i-Butane

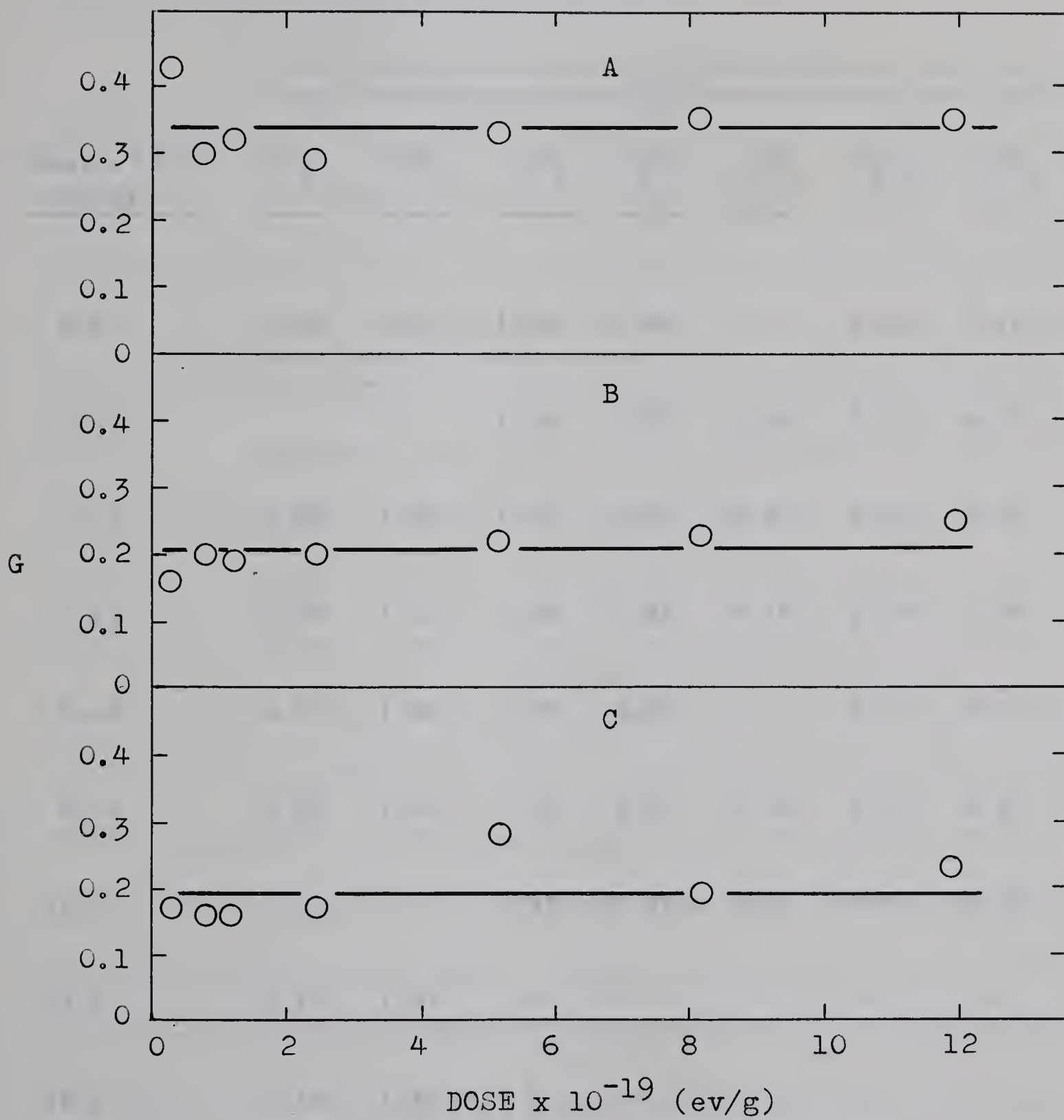






TABLE III-5

Yield of Gaseous Products as a Function of Dose

Dose x 10 <sup>-19</sup> (eV/g)	G							
	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>
0.27	4.98	1.61	1.38	0.88	-	0.43	0.16	0.17
0.77	-	-	1.62	0.97	0.30	0.30	0.20	0.16
1.12	5.45	1.29	1.55	0.93	0.31	0.32	0.19	0.16
2.44	5.24	1.28	1.40	0.86	0.38	0.29	0.20	0.17
5.14	5.31	1.42	1.47	0.91	-	0.33	0.22	0.28
8.11	5.25	1.24	1.39	0.91	0.26	0.35	0.23	0.19
11.9	-	-	1.39	0.88	0.11	0.35	0.25	0.23
13.0	5.16	1.31	-	-	-	-	-	-
18.1	5.12	1.24	-	-	-	-	-	-



consisted of a complex mixture of hydrocarbons ranging from  $C_4$  to greater than  $C_{14}$  compounds. Some of these products were formed in a very small yield, and were not identified.

The main liquid products were methylcyclohexene (MC),  $C_5$ - $C_6$ , and  $C_{14}$  hydrocarbons. The MC consisted of two partially resolved peaks on the chromatogram, the largest of which was identified as 1-methylcyclohexene (1-MC), the second peak which represented approximately 15% of the total MC contained both 3- and 4-methylcyclohexene (3- and 4-MC). Freeman (87) found that on a silica gel column, methylenecyclohexane (MEC) was completely isomerized to 1-MC. The isomers of MC were all measured together and were reported as total MC. Open chain heptenes came off the silica gel column between the MCH and 3- and 4-MC peaks, but at the highest doses used in the present study, all that was observed in this region of the chromatogram was a small irregularity on the tail of the MCH peak. The  $C_{14}$  products appeared as two peaks, the largest, 85% of the total, was assumed to be bi-methylcyclohexyl. The second  $C_{14}$  peak was not identified. The total dimer reported is the sum of these two products. The other large peak in the chromatogram was a poorly resolved doublet that came off the column just before the MCH. The retention times of saturated  $C_6$  hydrocarbon and  $C_5$  olefin were identical with this product doublet, but no positive identification was made. An impurity in the MCH (0.002%) before radiolysis had the same retention time; the amount of this impurity was subtracted from





the product peak before the yields were calculated. The yields of these products, referred to as unknown  $C_5-C_6$ , as a function of dose are presented in Table III-6 and Figure III-8.

The minor products that were found in the liquid analysis consisted of  $C_4$ ,  $C_5$  and  $C_9$  to  $C_{12}$  compounds and some high molecular weight products. The yield represented by the butane peak was combined with the butane measured in the  $-112^{\circ}$  fraction. The  $C_5$  region of the chromatogram contains three peaks which have retention times corresponding to saturated pentanes. Because the butenes which remain with the liquid products also have the same retention time as these  $C_5$  compounds, no reliable estimate of the  $C_5$  yield could be made. In between the MC and the dimer peaks were four small peaks which correspond to the region where  $C_9-C_{12}$  saturated hydrocarbons are eluted from the column. These peaks were broad and probably contained more than one component in each peak. Because of the small yield of these products ( $< 0.1$  G units) no identification was attempted. These unidentified products are referred to as unknown  $C_9-C_{12}$  A, B, C and D. In some samples, under favorable analytical conditions, two high molecular weight products were observed after the dimer peaks in the chromatogram. The yields of these products were small, in the range of 0.05 G units or less. They were identified only as high molecular weight products 1 and 2. Table III-6 presents the yields of these minor products. The extrapolated zero dose yields of the main products are given in Table III-7.



TABLE III-6

Yield of Liquid Products as a Function of Dose

Dose x 10 <sup>-19</sup> (eV/g)	G								
	Unk.	Total	Total	Unknown C <sub>9</sub> -C <sub>12</sub>				High Molecular	
	C <sub>5</sub> -C <sub>6</sub>	MC	C <sub>14</sub>	A	B	C	D	Weight Prod. 1	2
0.27	0.86	1.93	0.30	-	-	-	-	-	-
1.12	0.80	1.94	0.26	-	0.03	0.08	0.08	0.03	-
2.44	0.77	1.88	0.27	0.09	0.04	0.10	0.09	0.03	0.06
5.14	0.68	1.77	0.23	0.06	0.01	0.04	0.04	0.05	0.04
8.11	0.66	1.65	0.25	0.08	0.02	0.13	0.09	0.02	0.03
13.0	0.63	1.80	0.37	-	-	-	-	0.04	0.04
18.1	0.65	1.45	0.29	-	-	-	-	0.03	0.04

FIGURE III-8

Yields of Unknown C<sub>5</sub>-C<sub>6</sub>, Total MC, and Total Dimer  
as a Function of Dose

A: Unknown C<sub>5</sub>-C<sub>6</sub>

B: Total MC

C: Total Dimer

1000.000

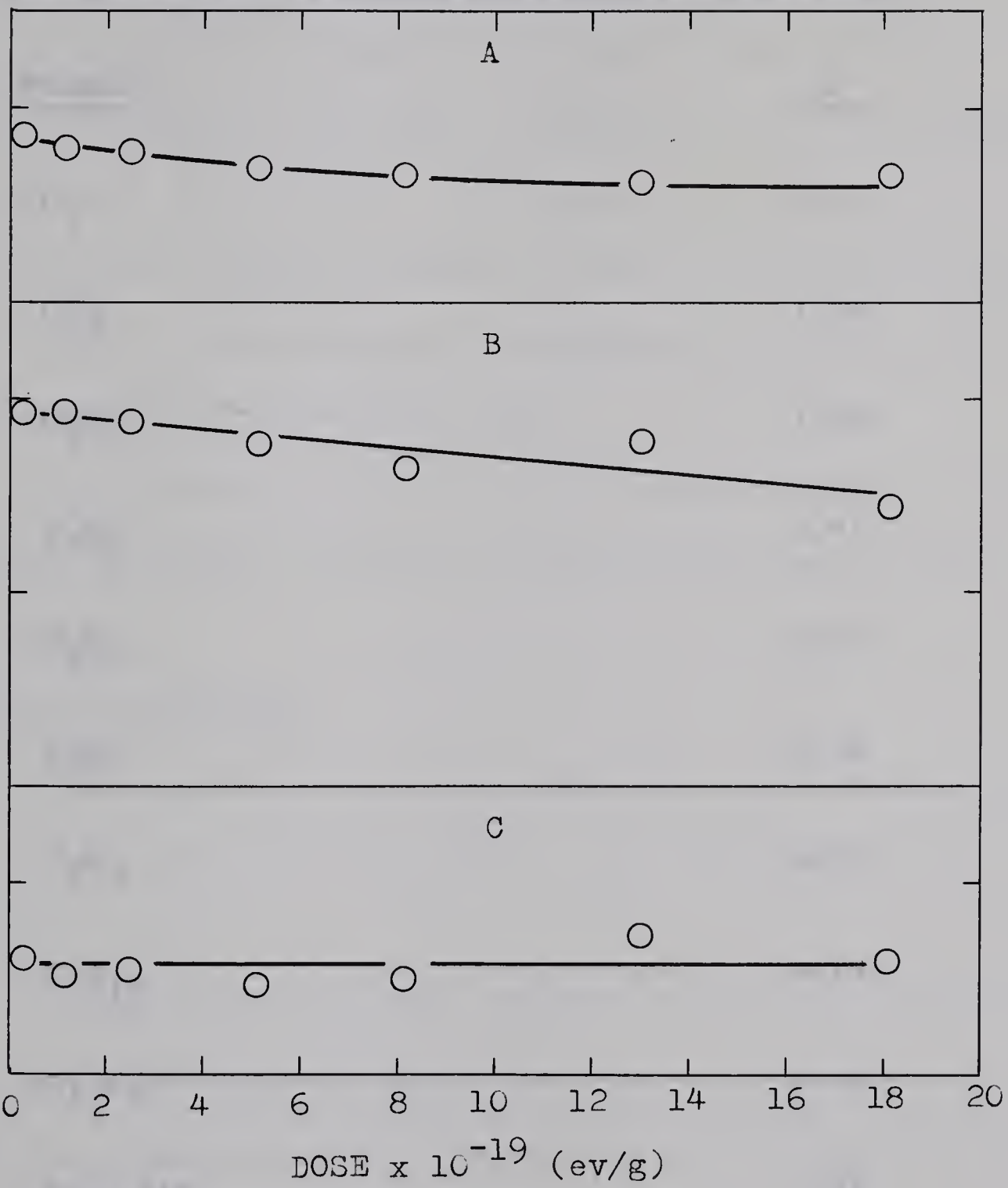






TABLE III-7

G-Values of Main Products Extrapolated to Zero Dose

<u>Product</u>	<u>G</u>
$H_2$	5.22
$CH_4$	1.34
$C_2H_4$	1.46
$C_3H_6$	0.91
$C_2H_2$	0.27
$C_2H_6$	0.34
$C_3H_8$	0.21
$C_4H_{10}$	0.19
$C_5-C_6$	0.90
Total MC	1.95
Total Dimer	0.28



## 2. Effect of Pressure

The effect of pressure on the yields of the radiolysis products from MCH vapor was determined over the range of 37 to 610 Torr. The pressure in the cells was changed by varying the amount of MCH in the cell from 0.08 grams to 1.28 grams. The temperature of the samples during irradiation was  $110 \pm 5^{\circ}\text{C}$ . All samples were given a dose of  $5 \times 10^{19}$  ev/gram of methylcyclohexane. Some of the minor products such as the  $\text{C}_9\text{-C}_{12}$  compounds and the high molecular weight products were not measured in this pressure study.

The G-values of products from the radiolysis of MCH vapor as a function of pressure are shown in Table III-8 and Figures III-9, III-10, and III-11.

## 3. Effect of Temperature

The temperature at which the MCH vapor was irradiated was varied over the range from  $60^{\circ}$  to  $260^{\circ}\text{C}$ . All major products were measured.

To keep the concentration of MCH constant in all samples, only 0.3 g of MCH was used so that it was all in the vapor state even at the lowest temperature ( $60^{\circ}\text{C}$ ). All samples were irradiated for the same length of time, giving them a constant dose of  $5 \times 10^{19}$  ev/gram of MCH.

The product yields as a function of temperature are presented in Table III-9 and Figures III-12, III-13, and III-14.





TABLE III-8Yield of Products from MCH as a Function of Pressure

Pressure (Torr)	<u>37</u>	<u>110</u>	<u>219</u>	<u>379</u>	<u>610</u>
<u>Product</u>	<u>G</u>				
H <sub>2</sub>	5.18	5.54	5.42	5.31	5.26
C <sub>2</sub> H <sub>6</sub>	0.50	0.34	0.33	0.39	0.34
C <sub>3</sub> H <sub>8</sub>	0.19	0.23	0.21	0.20	0.20
C <sub>4</sub> H <sub>10</sub>	0.22	0.20	0.21	0.20	0.24
Unknown C <sub>5</sub> C <sub>6</sub>	0.88	0.73	0.72	0.68	0.62
Total Dimer	0.23	0.32	0.30	0.23	0.34
CH <sub>4</sub>	1.84	1.67	1.66	1.57	1.20
C <sub>2</sub> H <sub>4</sub>	2.01	1.97	1.62	1.45	1.35
C <sub>3</sub> H <sub>6</sub>	1.04	0.99	1.00	0.92	0.85
Total MC	2.60	2.20	1.92	1.71	1.57

FIGURE III-9

Yields of Hydrogen, Ethane and Propane as a  
Function of Pressure

A:     Hydrogen

B:     Ethane

C:     Propane

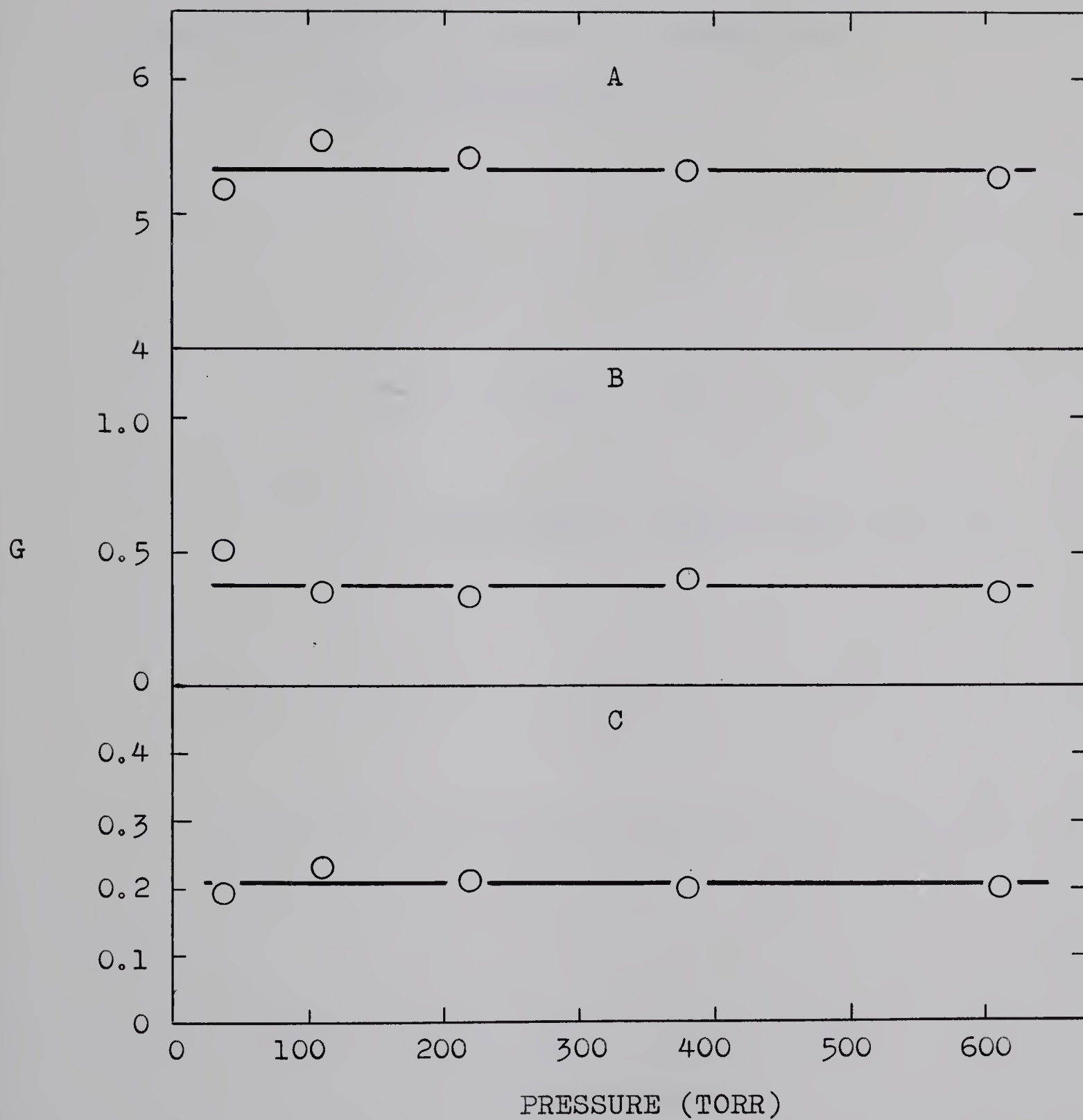


FIGURE III-10

Yields of Butane, Unknown C<sub>5</sub>-C<sub>6</sub> and Total Dimer  
as a Function of Pressure

A: n- + i-Butane

B: Unknown C<sub>5</sub>-C<sub>6</sub>

C: Total Dimer

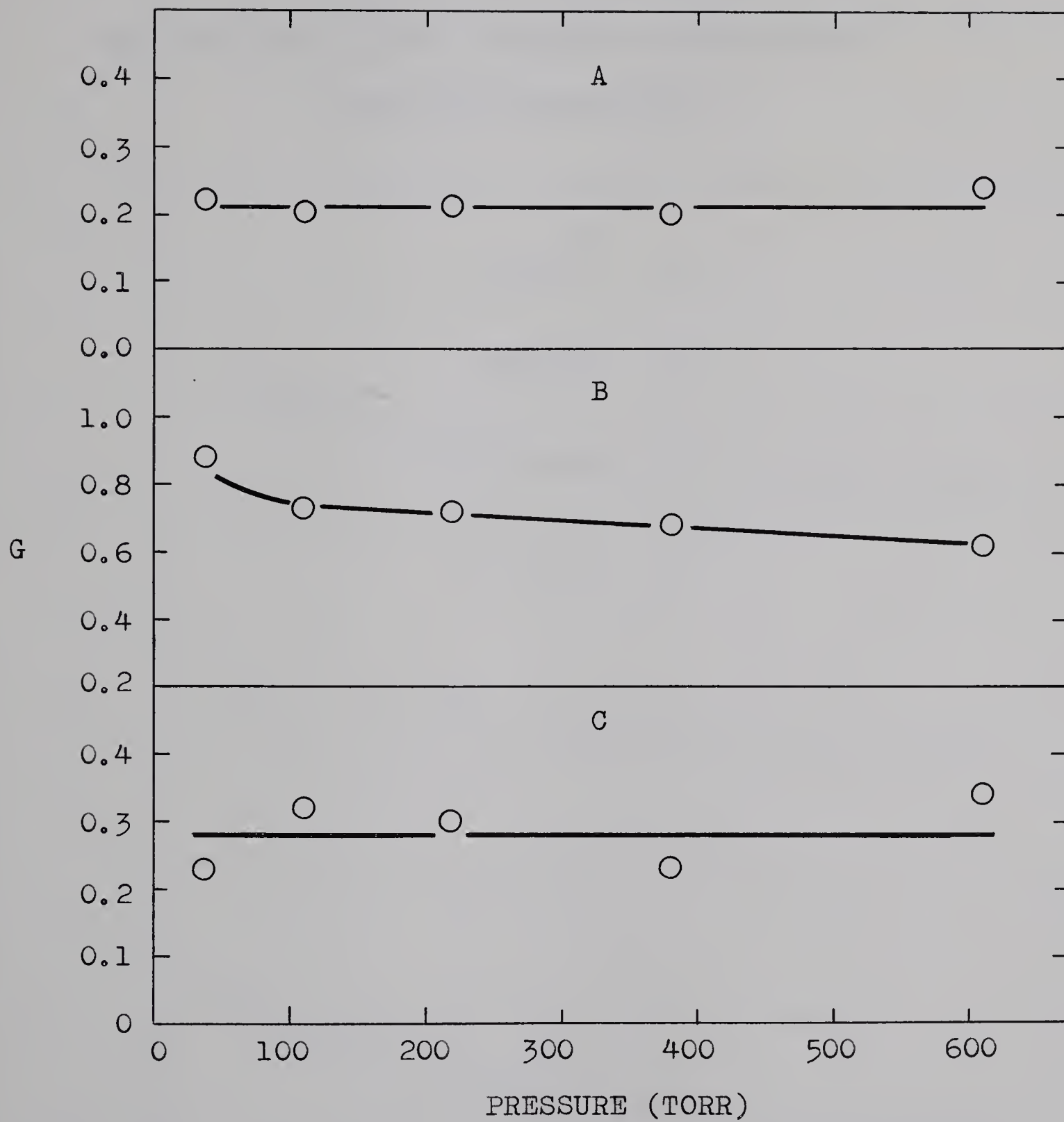




FIGURE III-11

Yields of Methane, Ethylene, Propylene and Total MC  
as a Function of Pressure

A: Methane

B: Ethylene

C: Propylene

D: Total MC

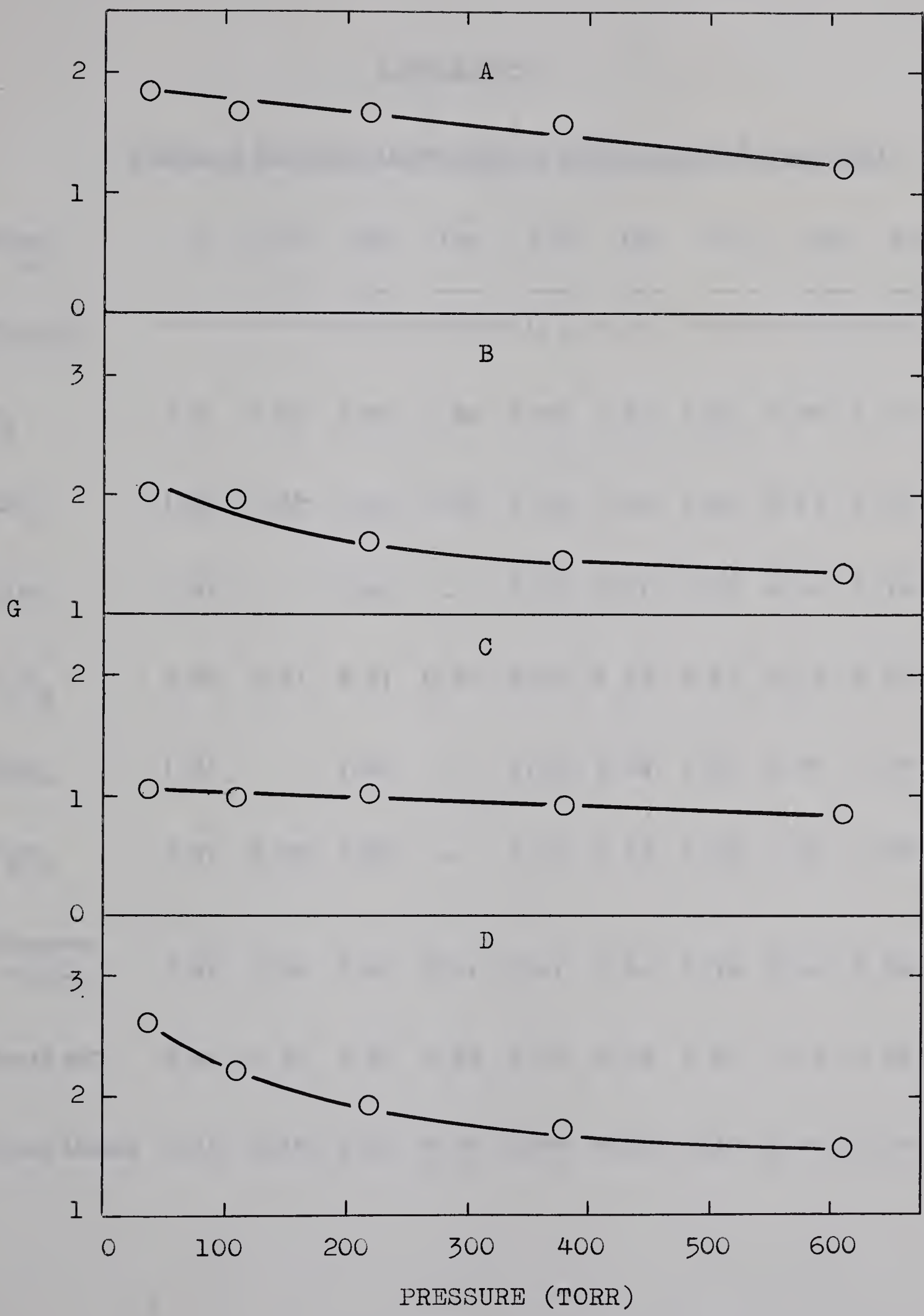




TABLE III-9Yields of Products from MCH as a Function of Temperature

Temp. °C	60	100	130	164	175	188	220	240	260
<u>Product</u>	<u>G</u>								
H <sub>2</sub>	4.94	5.52	4.85	5.84	5.26	5.83	5.60	5.90	6.33
CH <sub>4</sub>	1.40	1.43	1.62	1.69	1.69	1.96	2.20	2.15	2.91
C <sub>2</sub> H <sub>6</sub>	0.45	-	0.45	-	0.67	0.71	0.72	0.74	0.79
C <sub>3</sub> H <sub>8</sub>	0.30	0.23	0.21	0.25	0.26	0.25	0.23	0.27	0.29
C <sub>2</sub> H <sub>4</sub>	1.51	-	1.66	-	1.73	1.54	1.66	1.77	1.79
C <sub>3</sub> H <sub>6</sub>	0.99	0.95	1.09	-	1.25	1.10	1.35	1.31	1.58
Unknown C <sub>5</sub> -C <sub>6</sub>	0.58	0.64	0.65	0.67	0.61	0.65	0.78	0.64	0.86
Total MC	0.96	2.52	2.87	4.25	4.07	4.38	4.97	5.14	5.98
Total Dimer	0.18	0.18	0.32	0.18	0.09	0.16	0.34	0.16	0.30

FIGURE III-12

Yields of Hydrogen, Methane, Ethane and Propane  
as a Function of Temperature

A:     Hydrogen

B:     Methane

C:     Ethane

D:     Propane



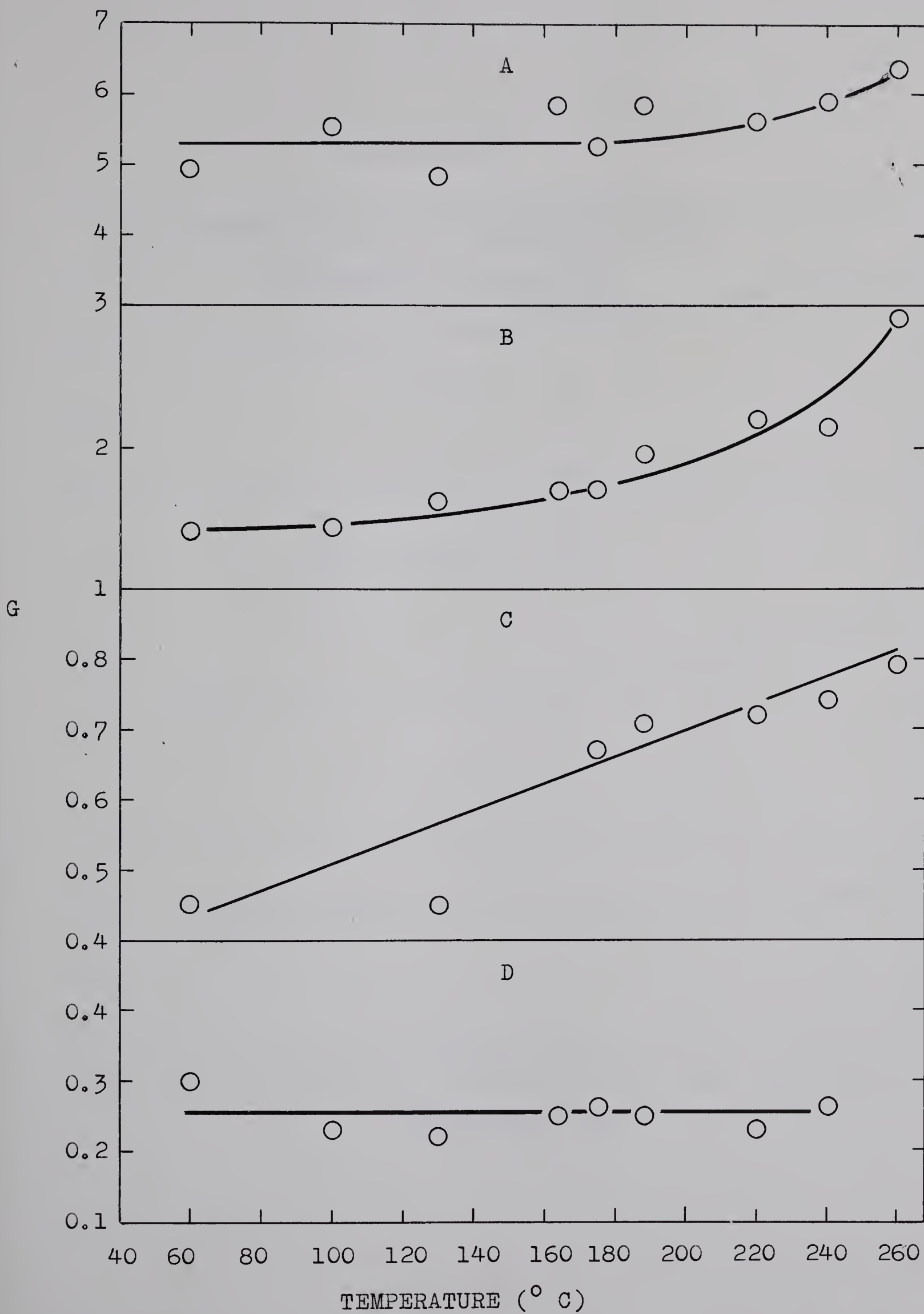


FIGURE III-13

Yields of Ethylene, Propylene, and Unknown C<sub>5</sub>-C<sub>6</sub>  
as a Function of Temperature

A: Ethylene

B: Propylene

C: Unknown C<sub>5</sub>-C<sub>6</sub>

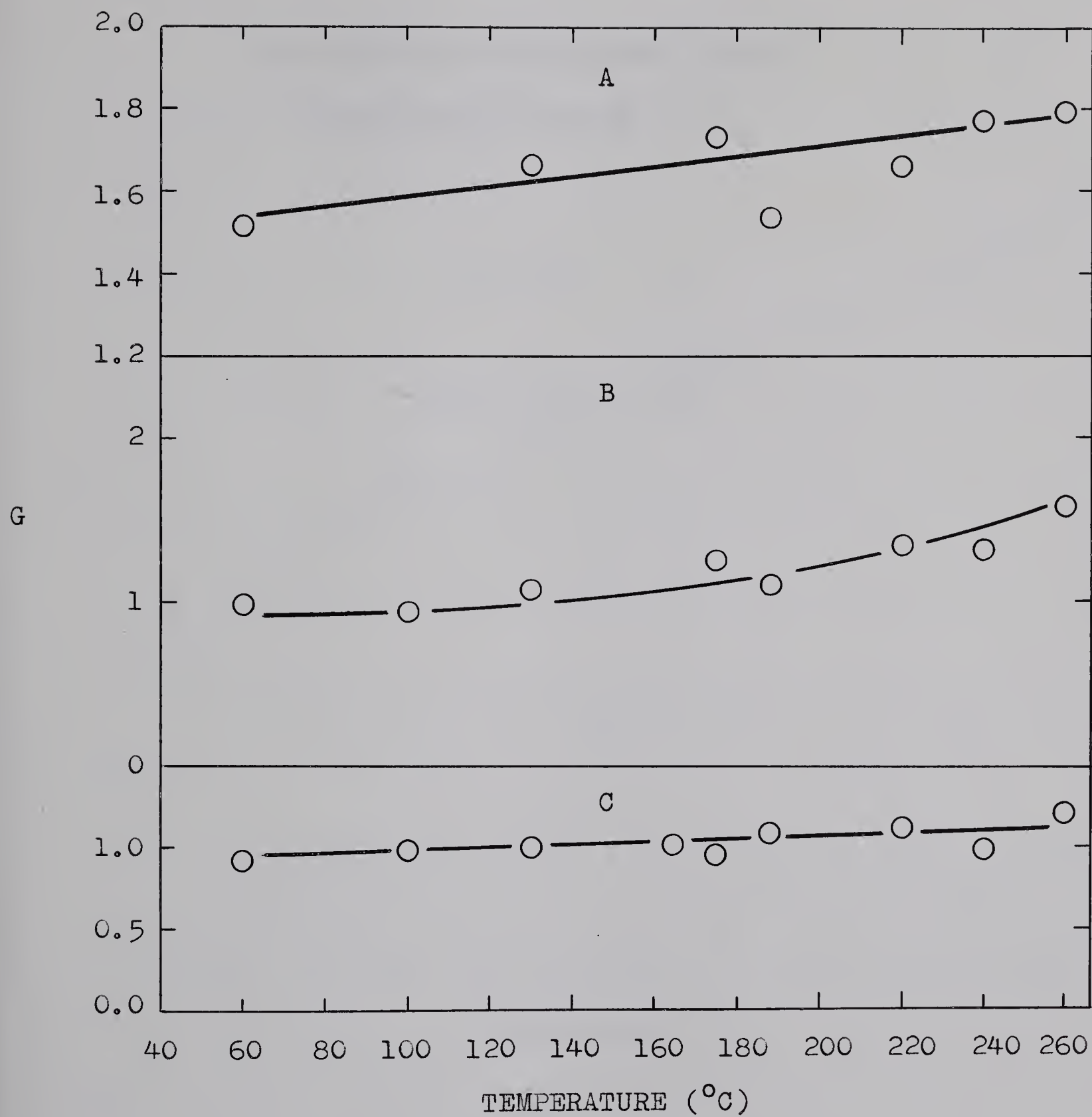
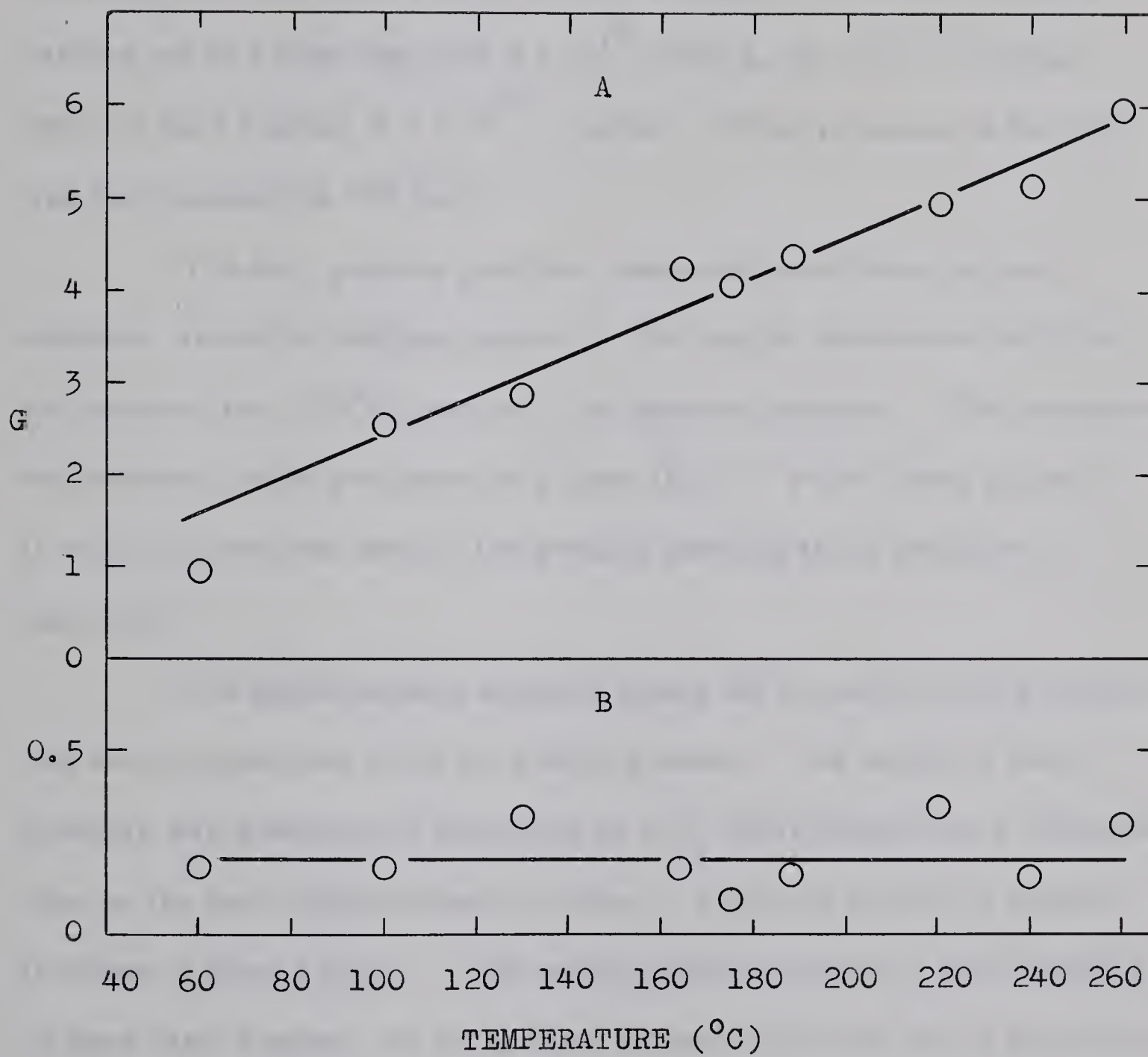


FIGURE III-14

Yield of Total MC and Total Dimer as a  
Function of Temperature

A: Total MC

B: Total Dimer







## D. Radiolysis of Methylcyclohexane Vapor Plus Additives

### 1. Methylcyclohexane-Ethylene

Binary mixtures of MCH vapor and ethylene were irradiated, covering the range from 0 to 70 percent ethylene. Irradiations were carried out at a dose rate of  $4.4 \times 10^{19}$  ev/hr g., at  $110^{\circ}\text{C}$  to a total dose for each sample of  $5 \times 10^{19}$  ev/gram. Total pressure in the cell was kept constant at 375 Torr.

The only gaseous products measured were hydrogen and methane, since the ethylene present in the sample interfered with the collection of the  $-112^{\circ}\text{C}$  fraction of the gaseous products. The hydrogen and methane yields are shown in Figure III-15. From these graphs it is seen that ethylene inhibits the process forming these products in pure MCH.

The liquid product analysis shows the formation of two products that are not observed in the pure MCH system. The larger of these products was qualitatively identified as a  $\text{C}_9$  hydrocarbon by its retention time on the gas chromatography column. The yield of this  $\text{C}_9$  product is shown in Figure III-16. The second additional product was identified as open chain heptene, by its position between MCH and MC on the chromatogram. Because this peak was on the tail of the MCH peak, the detection limit was high ( $\sim 0.3$  G units) and was not observed until the addition of 30 mole percent  $\text{C}_2\text{H}_4$ .

Above 30 mole percent  $\text{C}_2\text{H}_4$  the liquid products were so complex,

FIGURE III-15Yields of Hydrogen and Methane from  
MCH-Ethylene Mixtures

A :        Hydrogen

B :        Methane

(g = yield of product calculated from  
energy absorbed by MCH only)

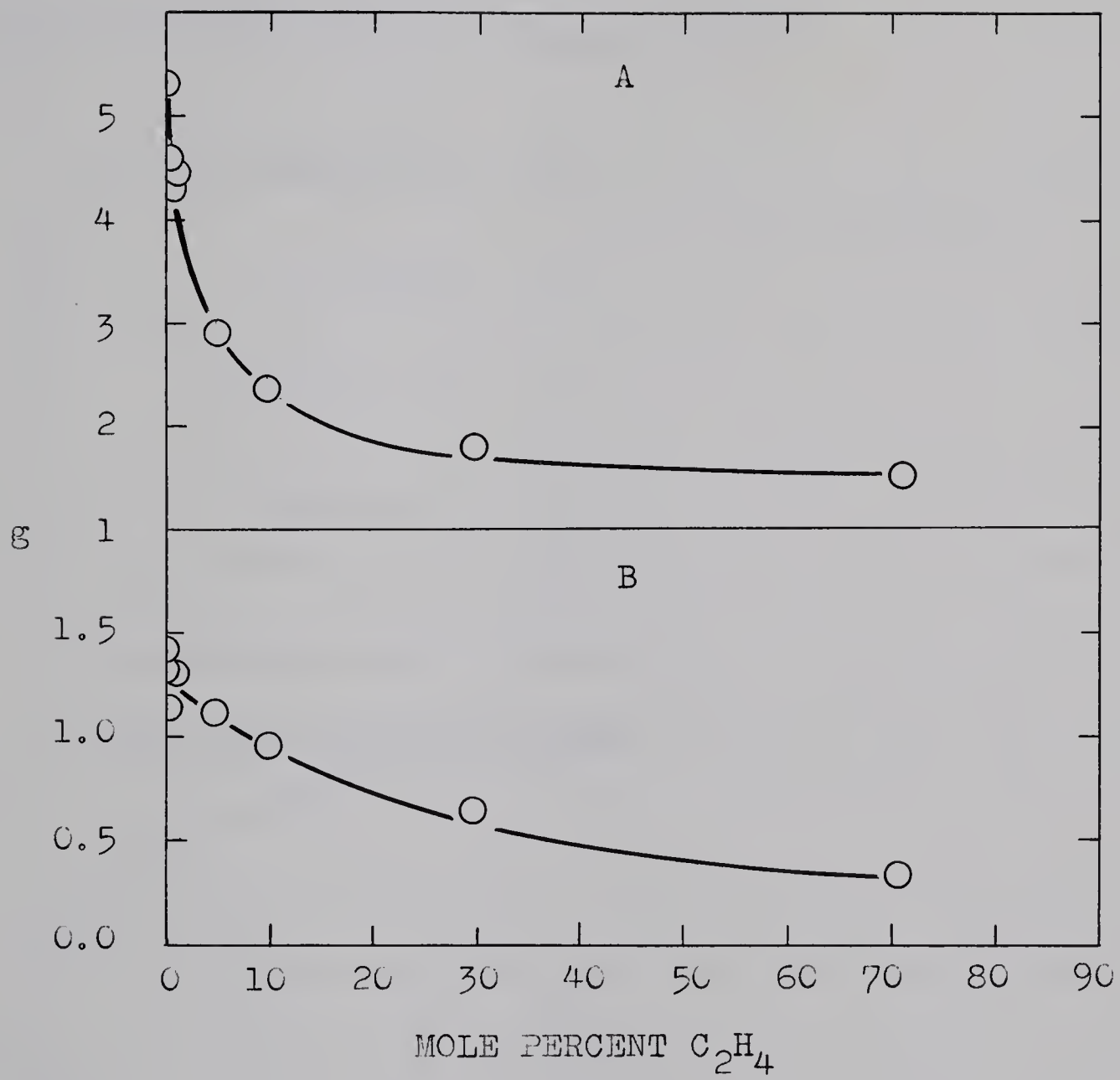


FIGURE III-16Yields of Liquid Products from MCH-Ethylene Mixtures

A:      Unknown C<sub>5</sub>-C<sub>6</sub>

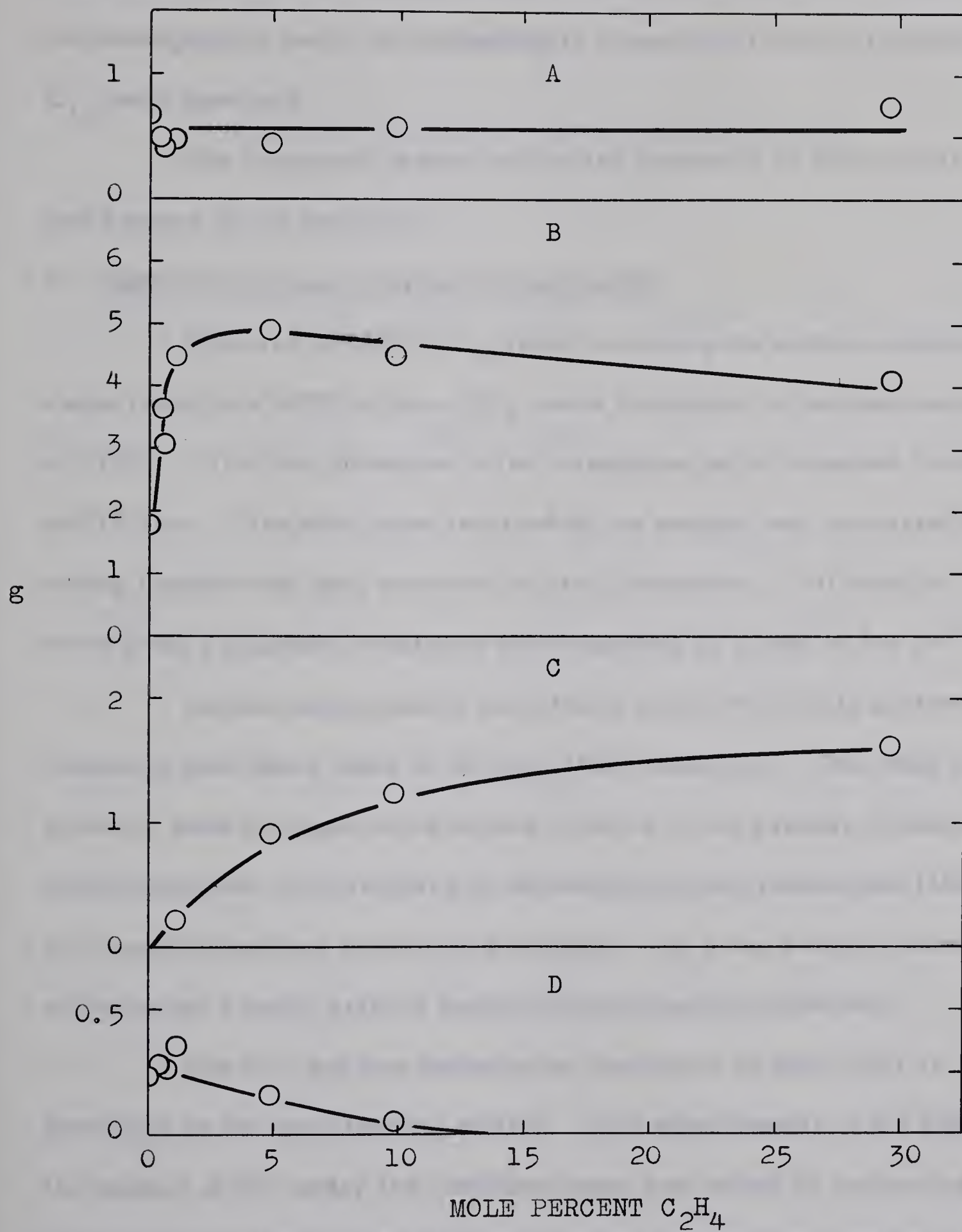
B:      Total MC

C:      C<sub>9</sub> - product

D:      Total Dimer

(g = yield of product calculated from  
energy absorbed by MCH only)







little attempt was made to quantitatively analyse the products. Gas chromatographic peaks corresponding to compounds from  $C_8$  to beyond  $C_{14}$  were observed.

The measured product yields are presented in Table III-10 and Figures III-15 and III-16.

## 2. Methylcyclohexane-Carbon Tetrachloride

Mixtures of  $MCH-CCl_4$  vapor, covering the entire concentration range from pure MCH to pure  $CCl_4$ , were irradiated in the Gammacell at  $110^\circ C$ . The total pressure in the irradiation cells remained constant at 375 Torr. The total dose received by the sample was calculated by adding together the dose received by each component. All samples were given a constant irradiation time resulting in a dose of  $6 \times 10^{19}$  ev/g.

Several new products were found in the  $MCH-CCl_4$  system, compared with those found in the pure MCH radiolysis. The main new products were hydrogen chloride and chlorine in the gaseous products, with chloroform, four isomers of the methylcyclohexylchlorides ( $MCCl$ ) and hexachloroethane in the liquid products. In some samples there was evidence for a small yield of methyltrichloromethylcyclohexane.

The  $HCl$  gas was analysed by absorption on solid  $KOH$  as described in the experimental section. The effectiveness of the  $KOH$  in removal of  $HCl$  under the conditions used was tested by measuring a known amount of  $HCl$  in the McLeod-Toepler combination, passing it through the  $KOH$  trap, and then remeasuring the residual gas. This test



TABLE III-10

Yields of Products from MCH-Ethylene Mixtures

<u>Mole Percent</u> <u>C<sub>2</sub>H<sub>4</sub></u>	<u>H<sub>2</sub></u>	<u>CH<sub>4</sub></u>	<u>Unknown</u> <u>C<sub>5</sub>-C<sub>6</sub></u>	<u>Open Chain</u> <u>Heptane</u>	<u>Total</u> <u>MC</u>	<u>C<sub>9</sub></u>	<u>Total</u> <u>Dimer</u>
0	5.31	1.42	0.68	-	1.77	-	0.23
0.533	4.58	1.33	0.47	-	3.66	-	0.27
0.608	4.31	1.13	0.43	-	3.09	-	0.26
1.06	4.43	1.32	0.48	-	4.48	0.23	0.35
4.86	2.91	1.12	0.44	-	4.90	0.91	0.16
9.88	2.36	0.96	0.57	-	4.54	1.24	0.04
29.6	1.78	0.65	0.75	0.54	4.13	1.62	-
70.7	1.53	0.34	-	-	-	-	-





indicated that 99% of the original HCl had been removed. Chlorine also can be absorbed on KOH pellets, and since it is volatile at  $-112^{\circ}\text{C}$  any  $\text{Cl}_2$  present in the radiolysis products was collected and measured with the HCl. In the  $-112^{\circ}$  fraction from pure  $\text{CCl}_4$  radiolysis, 95% of the gas was absorbed in the KOH; in addition a white precipitate was formed on the mercury surfaces in the analysis line. Chlorine is known to react rapidly with mercury (94). The large scatter in the  $\text{HCl-Cl}_2$  yields may be due to this reaction with mercury during analysis. For this reason, these yields must be considered only as estimates of the true yields.

The chromatogram at the  $-112^{\circ}\text{C}$  fraction<sup>also</sup> showed several new peaks, compared with the pure MCH system. These products were of low yield (approx. 0.2-0.4 G units total) and were not identified.  $C_a$  libration factors of known compounds in the same region of the chromatogram were assumed for measurement of the unidentified peaks. There were three distinct groups of new products. Group I consisted of four partially resolved peaks in the  $C_4$  region, immediately before the propylene peak; group II was on the tail of the propylene peak and also contained four peaks. Group II appeared only in mixtures of 50% or more  $\text{CCl}_4$ . The group III of unknown peaks had a retention time in the region of  $C_5$  hydrocarbons and contained five partially separated peaks. During the analysis of these products in the  $-112^{\circ}\text{C}$  fraction the characteristics of the silica gel column changed. As the



gaseous products from samples with increasing  $\text{CCl}_4$  concentration were analysed, the ethylene and propylene peaks began to tail badly, and their retention times increased. With this shift in retention time they interfered with the measurement of other peaks. Because of these difficulties the scatter in the yield of the  $-112^\circ$  fraction products were large.

The new liquid products formed in the radiolysis of the MCH- $\text{CCl}_4$  mixtures were identified by peak reinforcement with authentic samples of these compounds on several columns. Chloroform and hexachloroethane were commercially available. Methylcyclohexylchloride was prepared by reaction of concentrated hydrochloric acid with 1-MC at  $100^\circ$  for two hours (95). The analysis of the liquid products from the MCH- $\text{CCl}_4$  radiolysis showed two doublet peaks in the region where the synthetic  $\text{MCCl}$  came off the column. Each doublet contained one large peak with a small peak partially resolved from it. The prepared  $\text{MCCl}$  had a retention time identical to the large peak in the first doublet. These doublets are referred to as  $\text{MCCl-1}$  and  $\text{MCCl-2}$  since their exact structure was not determined. The dimer peaks were very small on this chromatograph and consisted of two partially separated peaks. These were measured together to give the total dimer yield. Between the  $\text{C}_2\text{Cl}_6$  and  $\text{C}_{14}$  peaks were two small peaks that were assumed to be isomers of methyltrichloromethylcyclohexane.

The gaseous and liquid product yields obtained from the







irradiation of MCH-CCl<sub>4</sub> mixtures in the vapor phase are tabulated in Tables III-11 and III-12 and illustrated in Figures III-17 to III-21.

### 3. Methylcyclohexane-Nitrous Oxide

#### a. Radiolysis of MCH-N<sub>2</sub>O Mixtures as a Function of N<sub>2</sub>O Concentration

The radiolysis of MCH-N<sub>2</sub>O mixtures were studied from 0 to 10 mole percent nitrous oxide. These irradiations were done in the Gammacell at 110°C; the total dose absorbed by each sample was  $5 \times 10^{19}$  ev/g. The yields of products as a function of nitrous oxide concentration were measured at four different total pressures - 50, 150, 375 and 520 Torr. Product yields as a function of N<sub>2</sub>O concentration at 50°C and 125 Torr pressure, were also measured.

The -210° fraction of the gaseous products from this system contained three additional products that were not observed in the pure MCH radiolysis. The largest of these was nitrogen with only small amounts of oxygen (~0.05 G units) and approximately 0.01 G units of an unidentified product, which is probably carbon monoxide or nitric oxide.

These products were separated on a molecular sieve (13 X) column and were eluted from the column in the order of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> and unknown. A thermal conductivity detector was necessary for this analysis since the hydrogen flame detector was not sensitive to the inorganic gases. The C<sub>2</sub>-C<sub>4</sub> products were not measured because of interference of N<sub>2</sub>O which was volatile at -112°C.

The liquid products were analysed on the flame ionization



TABLE III-11

Yields of Gaseous Products from MCH-Carbon Tetrachloride Mixtures

G										
Mole % CCl <sub>4</sub>	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	HCl +Cl <sub>2</sub>	Unknown		
								Group I	II	III
0	5.31	1.42	0.33	0.22	1.47	0.91	-	-	-	-
0.17	3.37 (3.37)*	1.24	0.37	0.24	1.51	0.87	-	-	-	-
0.112	3.17 (3.17)	1.27	0.30	0.15	1.07	0.34	4.37	0.06	-	0.10
0.171	3.18 (3.19)	1.15	0.29	0.15	1.02	0.55	4.33	0.08	-	0.17
0.762	3.07 (3.10)	1.24	0.23	0.12	1.05	0.66	4.68	0.11	-	0.20
1.34	2.96 (3.00)	1.28	0.34	0.15	1.44	0.82	-	-	-	-
4.11	2.92 (3.06)	1.06	0.22	0.09	0.77	0.48	6.14	0.07	-	0.12
6.57	2.91 (3.15)	1.02	0.33	0.12	1.47	0.75	-	-	-	-
7.82	2.66 (2.93)	1.12	0.24	0.09	0.98	0.60	5.30	0.08	-	0.13
12.0	2.51 (2.91)	1.05	0.20	0.08	0.88	0.50	6.86	0.11	-	0.16
16.4	2.21	0.94	0.22	0.08	0.85	0.52	5.72	0.07	-	0.13
28.8	1.73	0.82	0.17	0.08	0.72	0.36	7.59	0.06	-	0.08
32.9	1.70	0.95	0.18	-	0.87	0.34	7.49	-	-	-
43.7	1.19	0.78	0.12	0.06	0.62	0.35	9.26	0.11	0.06	0.22
63.2	0.58	0.59	0.08	0.01	0.49	0.24	9.15	0.08	0.09	0.16
89.3	0.09	0.21	0.03	0.02	0.14	0	12.3	0.04	0.19	0.08
100	0	0	0	0	0	0	12.6	-	-	-

\*Values in brackets are H<sub>2</sub> yields calculated on basis of energy absorbed by MCH only.



TABLE III-12

Yields of Liquid Products from MCH-Carbon Tetrachloride Mixtures

Mole Percent $\text{CCl}_4$	G						
	$\text{CHCl}_3$	Total MC	MCHCl-1	MCHCl-2	$\text{C}_2\text{Cl}_6$	$\text{CCl}_3\text{-C}_7\text{H}_{13}$	Total $\text{C}_{14}$
0	-	1.77	-	-	-	-	0.23
0.112	6.5	2.54	2.10	1.67	0.13	-	0.21
0.171	10.2	2.52	3.22	2.76	-	-	0.36
0.762	22.6	4.82	6.17	11.1	0.53	-	0.51
4.11	34.4	5.83	8.12	17.7	1.99	-	0.56
7.82	34.9	4.24	11.4	19.3	2.59	-	0.65
12.0	40.0	3.54	16.9	24.2	3.07	0.1	0.75
16.4	39.6	3.56	17.6	24.5	3.54	0.1	0.45
28.8	33.6	2.51	18.3	22.9	4.25	0.1	0.25
43.7	34.3	2.21	15.7	23.0	5.67	0.3	0.29
63.2	24.6	1.71	11.3	19.8	6.51	0.3	0.10
89.3	11.8	1.19	5.35	13.6	-	-	-
100	-	-	-	-	-	-	-



FIGURE III-17

Yields of Hydrogen, Methane, Ethane and Propane from  
MCH-Carbon Tetrachloride Mixtures

- A:      Hydrogen
- B:      Hydrogen (expanded scale.    g: yield based  
         on energy absorbed by MCH only)
- C:      Methane
- D:      Ethane
- E:      Propane

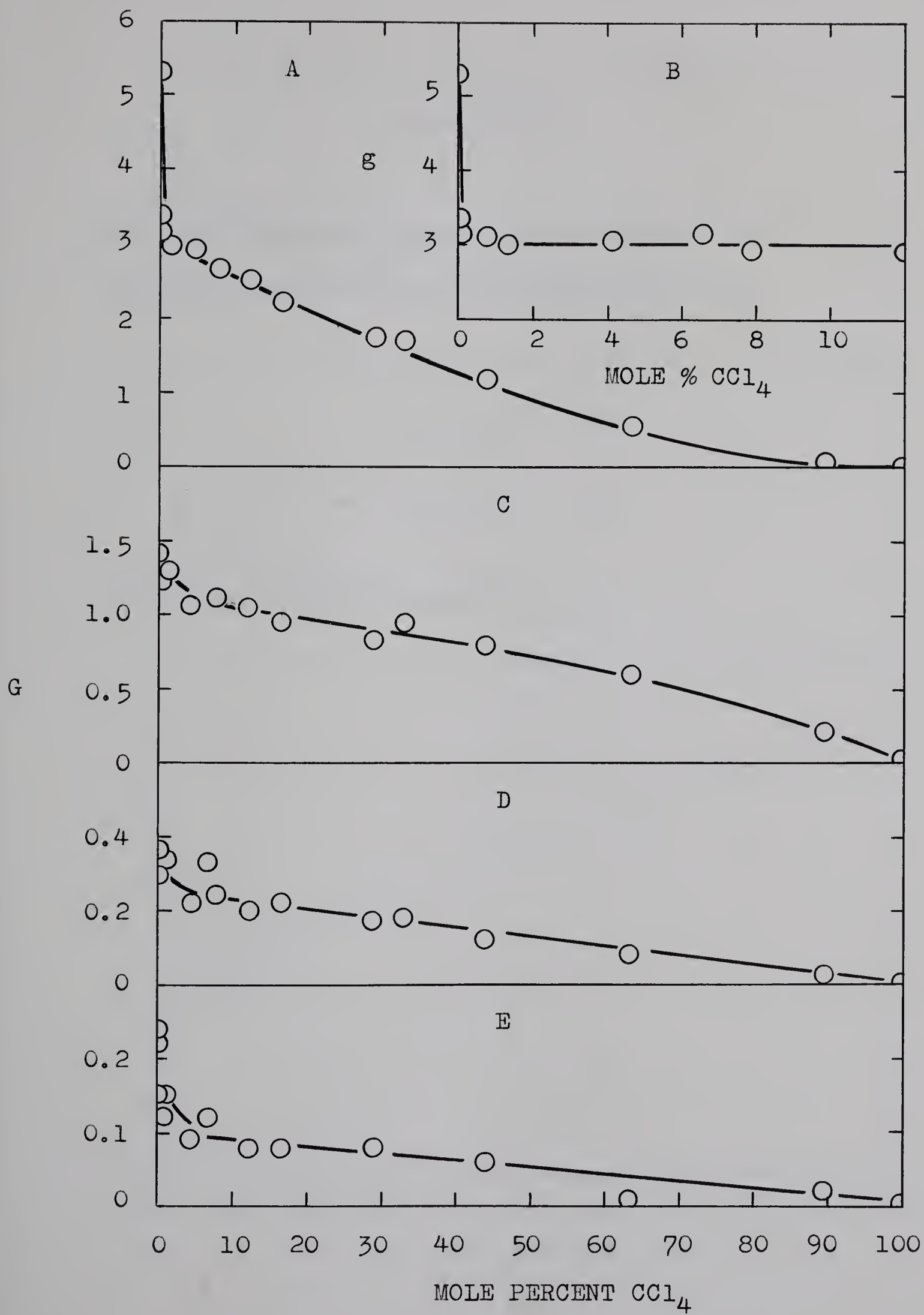


FIGURE III-18

Yield of Ethylene, Propylene and Hydrogen Chloride plus  
Chlorine from MCH-Carbon Tetrachloride Mixtures

A: Ethylene

B: Propylene

C: Hydrogen Chloride plus Chlorine

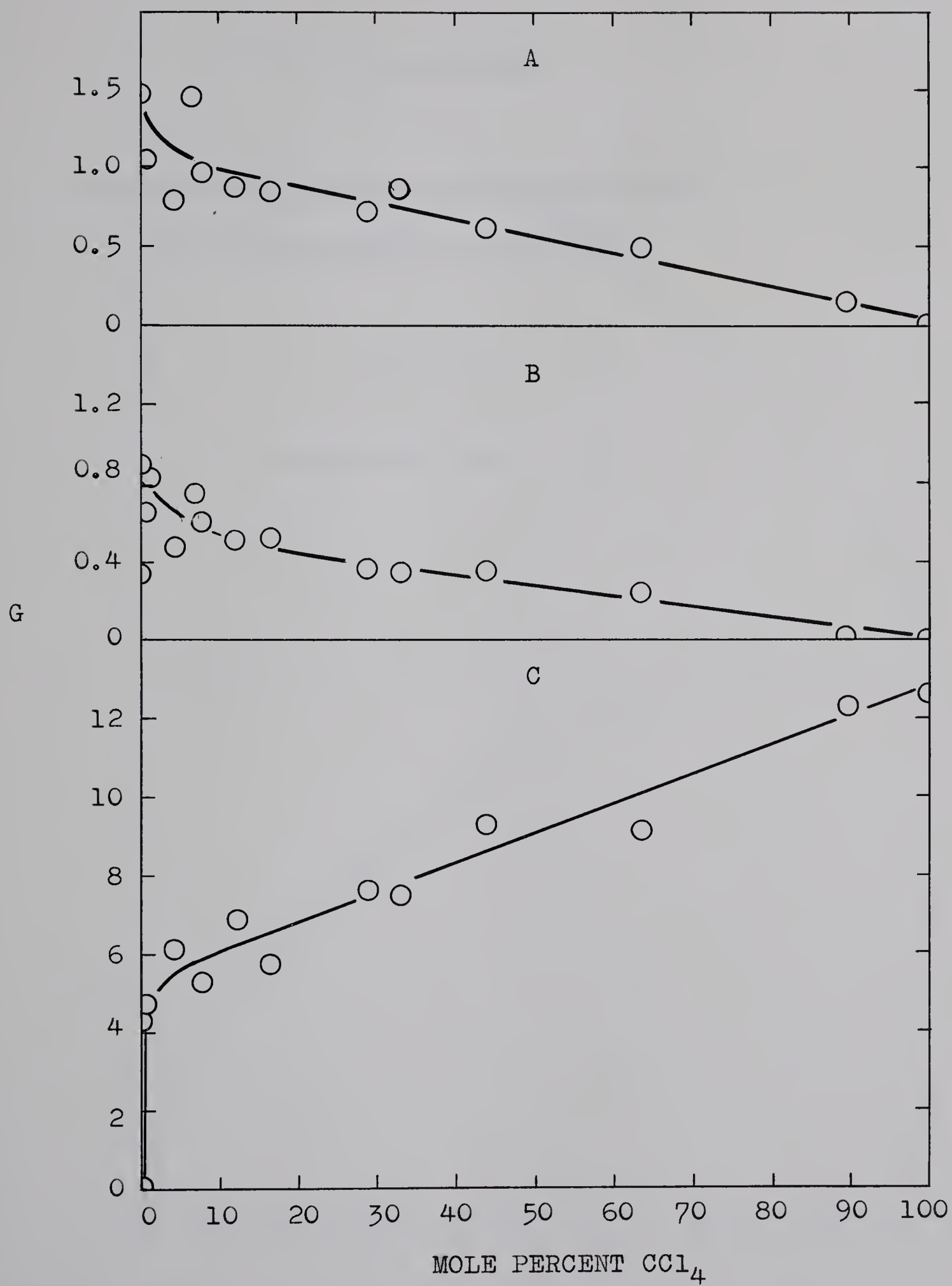


FIGURE III-19

Yield of Chloroform and Hexachloroethane from  
MCH-Carbon Tetrachloride Mixtures

A: Chloroform

B: Hexachloroéthane



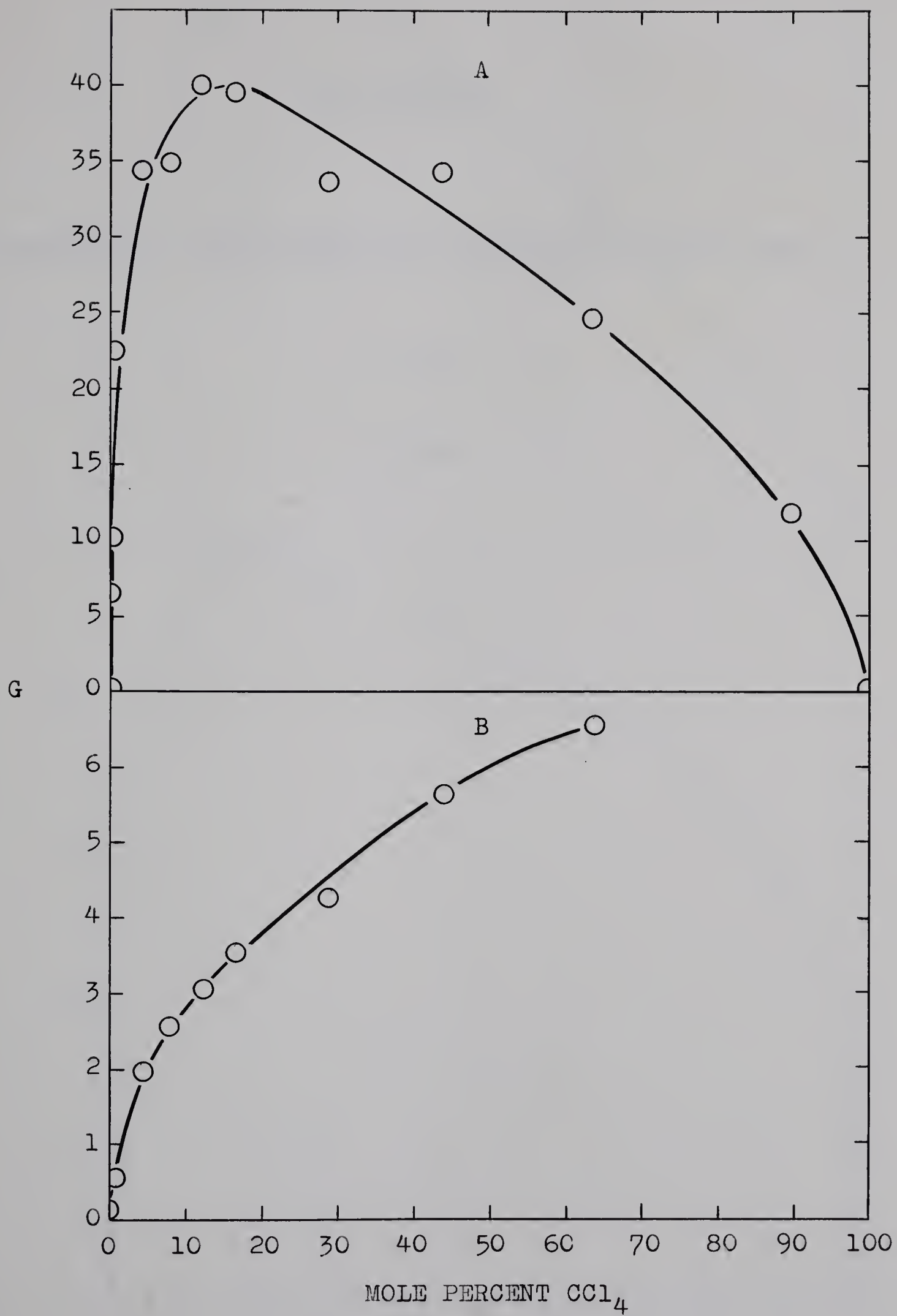


FIGURE III-20

Yield of MCCl - 1 and MCCl - 2 from MCH-Carbon Tetrachloride Mixtures

A:      MCCl - 1

B:      MCCl - 2

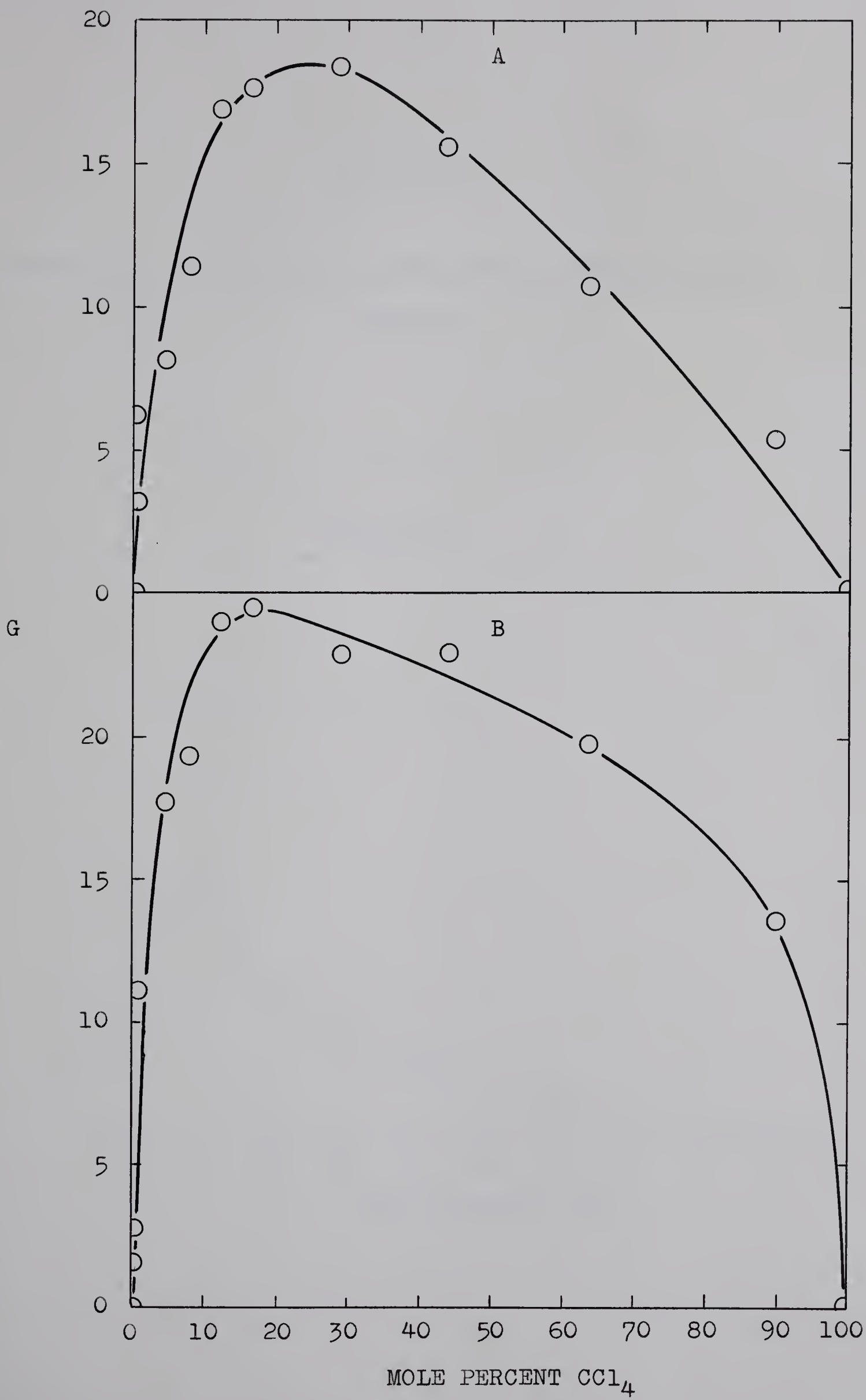


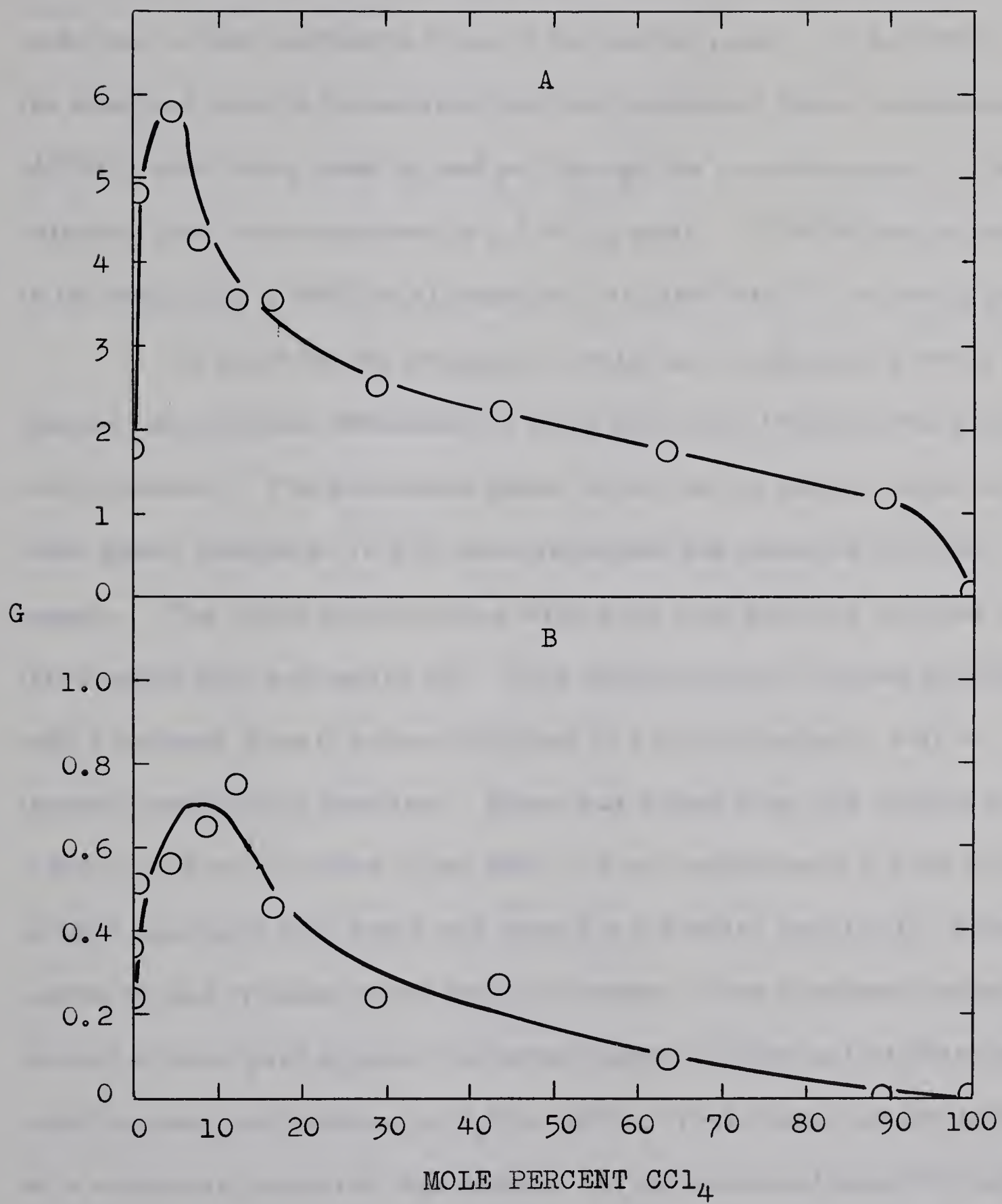
FIGURE III-21

Yields of Total MC and Total Dimer from MCH-Carbon Tetrachloride

Mixtures

A: Total MC

B: Total Dimer







chromatograph. The presence of methylcyclohexyl alcohol (MCOH) in the liquid products was anticipated but analysis of the liquid products on a Ucon column showed no trace of the alcohol peak. To determine the detection limit of the analysis for this compound, dilute solutions of MCOH in MCH were made up and put through the chromatograph. The detection limit was equivalent to 0.2-0.3 g units. If MCOH was a product in the radiolysis of MCH-N<sub>2</sub>O mixtures, its yield was 0.3 or less g units.

To check for the presence of water as a radiolysis product a special sample which contained 0.1 ml of MCH with 10% N<sub>2</sub>O was prepared and irradiated. The permanent gases as well as the nitrous oxide and other gases volatile at -112°C were separated and removed from the sample. The liquid products plus MCH were then distilled from the cell into a small bulb and sealed off. This small bulb was crushed directly onto a Poropak Type Q column installed in a chromatograph, with a thermal conductivity detector. Water was eluted from this column as a sharp peak well in front of the MCH. For comparison a 0.1 ml solution of MCH saturated with water was placed in a similar small bulb, degassed, sealed off and crushed on the Poropak column. The irradiated sample showed a water peak greater than three times as large as that observed from the saturated solution of H<sub>2</sub>O in MCH. Thus water was identified as a radiolysis product in this system, but not measured quantitatively.

The yields of the products measured from the radiolysis of N<sub>2</sub>O in MCH are presented in Table III-13 and Figures III-22 and III-23.



TABLE III-13

Yields of Products from MCH-Nitrous Oxide Mixtures





Mole % N <sub>2</sub> O	Temp. °C	Press. (Torr)	g				Total MC	Total Dimer
			H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	Unk. C <sub>5</sub> -C <sub>6</sub>		
0	110	50	5.35	-	-	0.80	2.50	0.23
9.3 x 10 <sup>-2</sup>	110	58	3.79	4.93	-	0.86	5.13	0.56
1.00	110	51	3.24	15.2	-	0.54	12.4	1.43
7.51	110	54	3.42	20.3	-	0.73	15.4	0.95
<hr/>								
0	110	152	5.42	-	-	0.71	2.10	0.31
0.10	110	148	3.46	7.66	-	0.77	5.57	0.87
1.84	110	152	3.32	21.6	-	0.54	15.1	1.72
2.14	110	150	3.23	22.2	-	-	-	-
6.61	110	148	3.33	23.2	-	0.70	17.0	0.86
<hr/>								
0	110	379	5.31	-	1.42	0.68	1.77	0.23
9.7 x 10 <sup>-3</sup>	110	379	5.35	0.32	1.20	0.66	2.30	0.33
8.8 x 10 <sup>-2</sup>	110	374	3.24	8.92	1.07	0.72	7.07	0.88
0.102	110	392	3.19	10.5	1.42	0.84	7.57	1.00
1.00	110	380	3.07	19.6	1.23	0.61	13.9	0.84
1.95	110	374	3.04	21.2	1.09	0.75	15.7	1.61
4.88	110	374	3.20	21.6	1.22	0.90	15.8	1.29
6.98	110	374	2.96	22.6	1.11	-	16.3	1.60
9.83	110	349	3.18	22.6	1.30	0.72	18.0	1.79
<hr/>								
0	110	519	5.26	-	1.20	0.62	1.57	0.34
9.8 x 10 <sup>-2</sup>	110	527	3.15	9.95	1.21	0.74	6.91	1.19
9.98	110	518	2.98	20.9	1.10	0.62	15.5	1.60
<hr/>								
0	60	125	4.94	-	-	-	0.96	0.18
0.102	50	122	3.62	3.40	-	-	0.76	0.55
2.12	51	124	3.39	15.7	-	-	7.21	0.63
6.64	50	124	3.44	21.4	-	-	11.7	0.75
10.5	50	124	3.08	24.0	-	-	10.7	0.79

FIGURE III-22Yields of Hydrogen and Nitrogen from MCH-  
Nitrous Oxide Mixtures


A:      Hydrogen

B:      Nitrogen

Open Symbols - Irradiation at 110°C

:      50 Torr:      150 Torr:      375 Torr:      520 Torr

Filled Symbols - Irradiation at 50°C

:      124 Torr



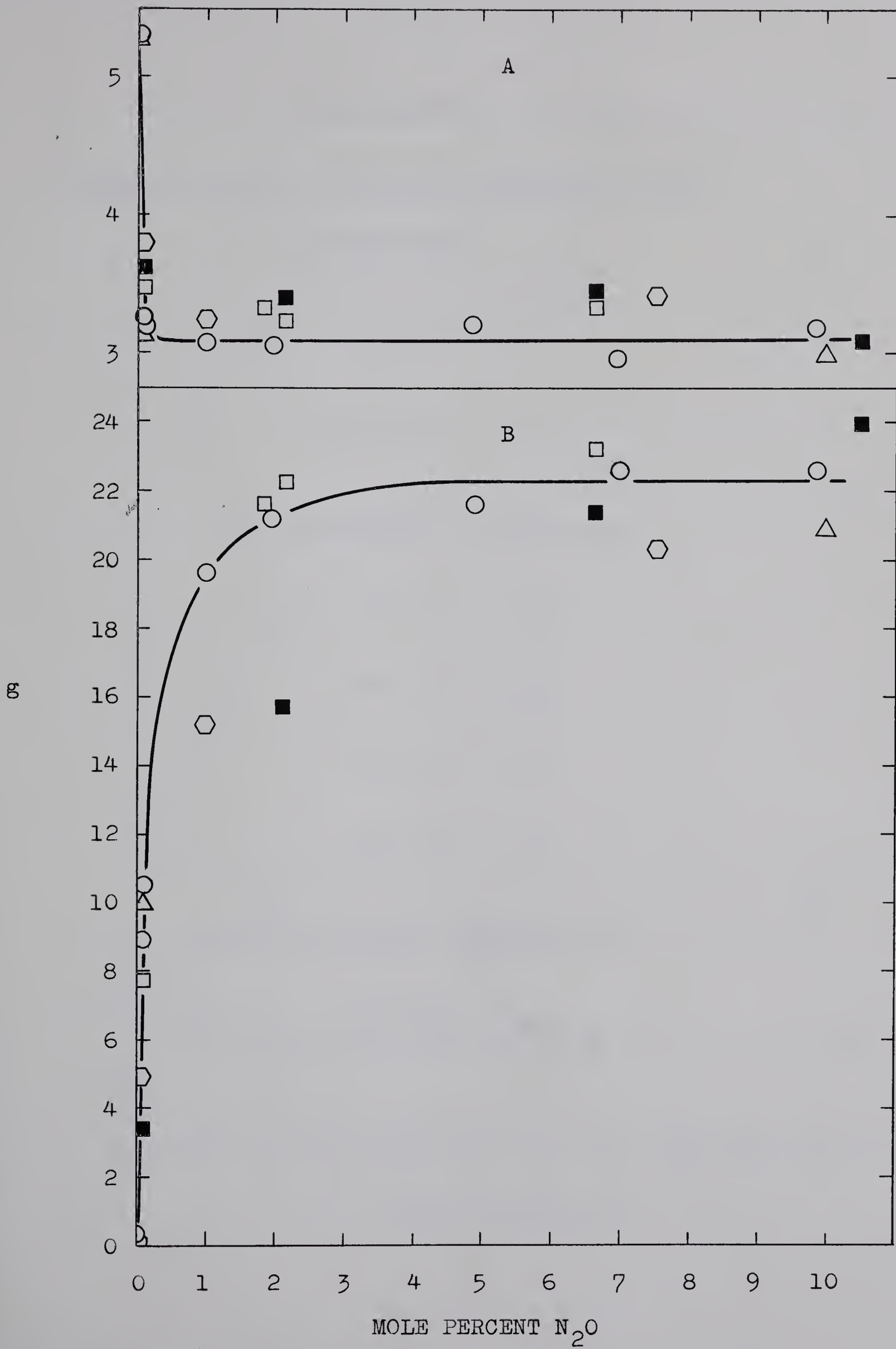


FIGURE III-23

Yields of Total MC and Total Dimer from MCH-Nitrous  
Oxide Mixtures

A: Total MC

B: Total Dimer

Open Symbols - Irradiation at 110°C

⬡: 50 Torr

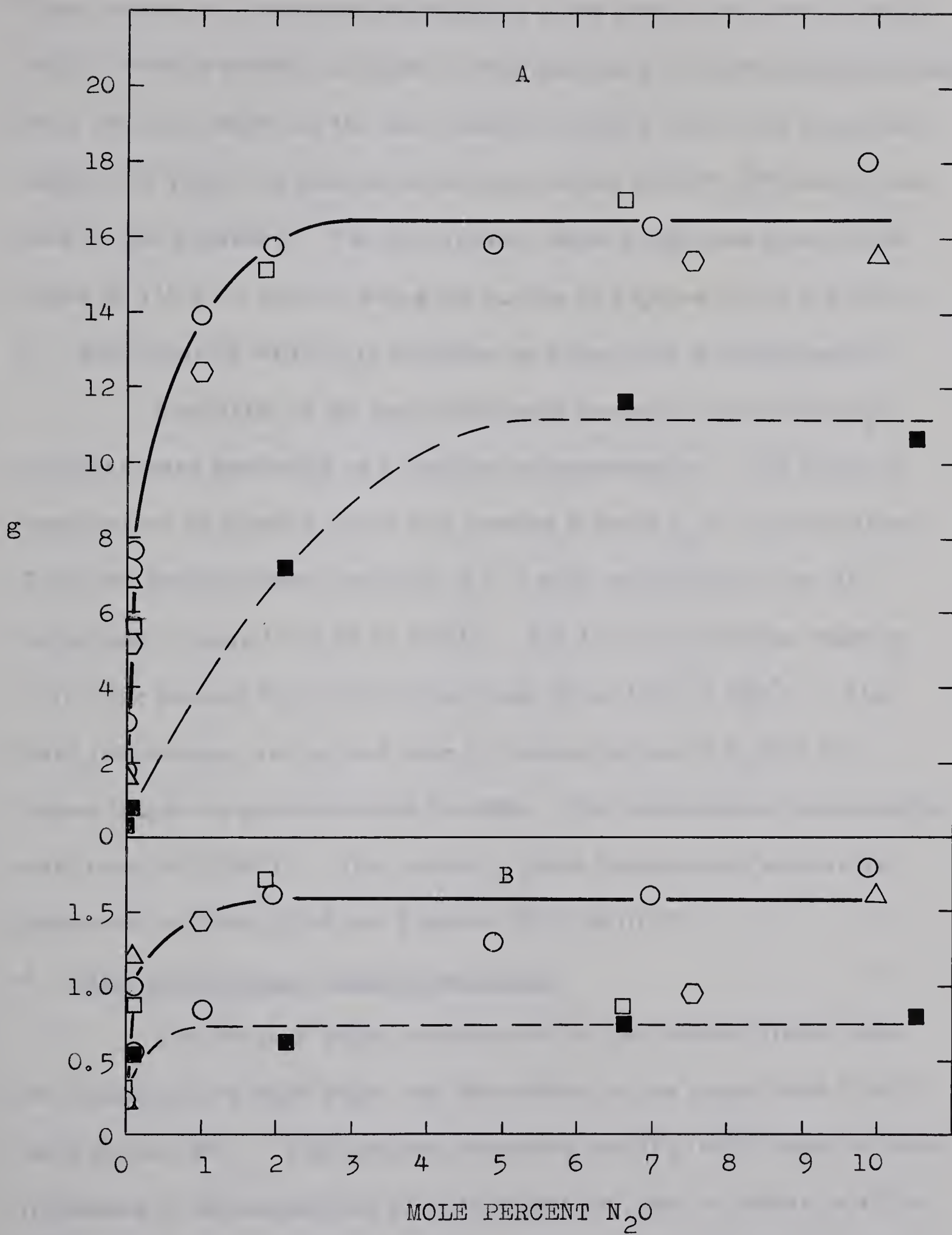
□: 150 Torr

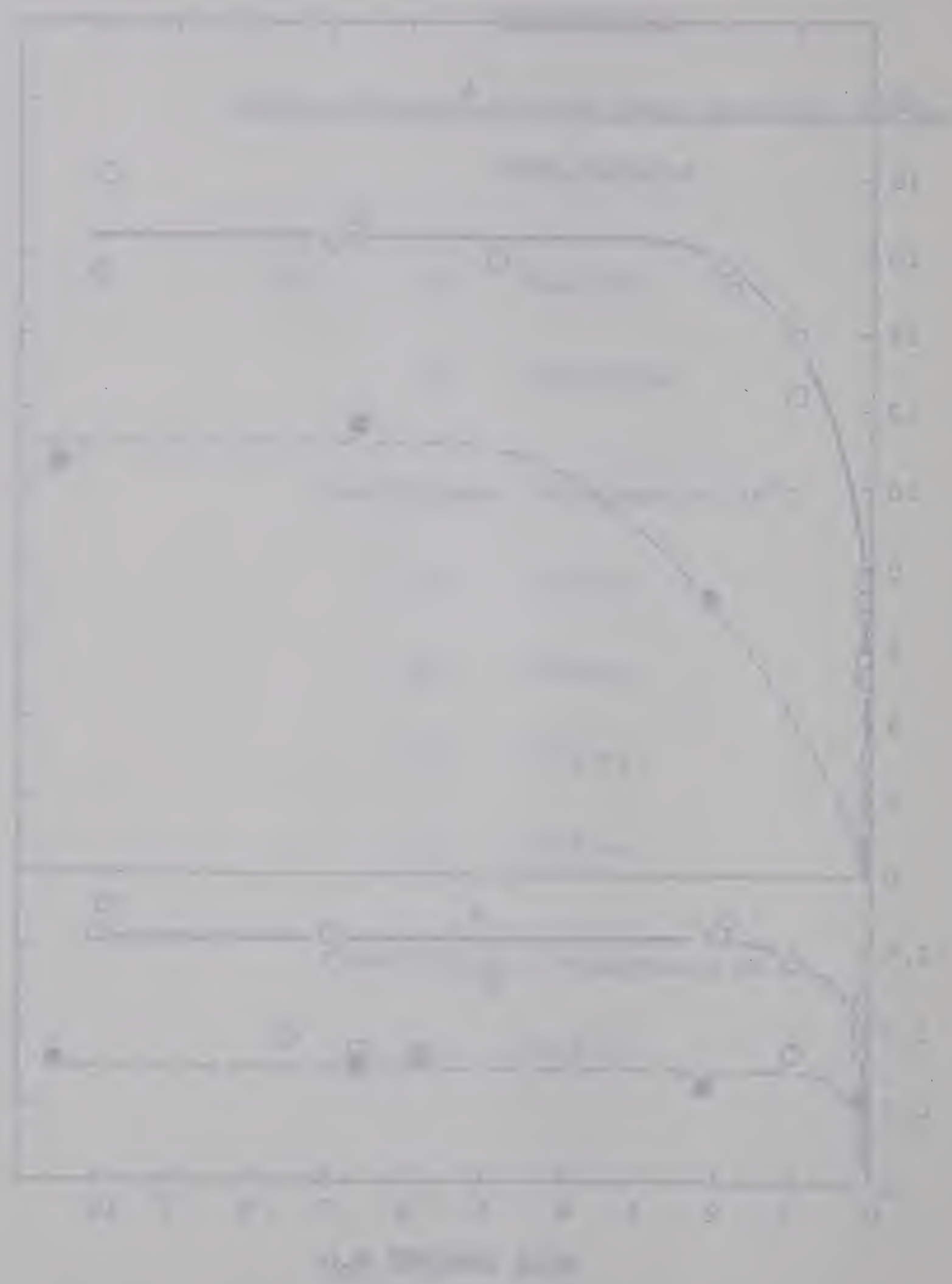
○: 375 Torr

△: 520 Torr

Filled Symbols - Irradiation at 50°C

■: 124 Torr





These yields are calculated on the basis of the energy absorbed by MCH only. Product yields calculated on this basis are given the symbol  $g(\text{prod})$ . Since the dose study and the other additive studies were done at approximately 375 Torr, the most detailed study of the MCH-N<sub>2</sub>O mixtures was done at this pressure. For this reason, most weight was given to the points at 375 Torr when drawing the curves in Figures III-22 and III-23.

#### b. Radiolysis of MCH-N<sub>2</sub>O Mixtures as a Function of Temperature

The yields of the main radiolysis products from MCH-N<sub>2</sub>O mixtures were measured as a function of temperature. The effect of temperature on product yields was studied at three N<sub>2</sub>O concentrations. The most detailed study was done at 0.5 mole percent N<sub>2</sub>O over the temperature range from 60 to 225°C. The low concentration study at 0.01 mole percent N<sub>2</sub>O covered the range from 110°C to 200°C. The third temperature series was done at concentrations of N<sub>2</sub>O in the plateau region of product yields (2-10%). The temperature range studied was from 50 to 200°C. The results of these temperature studies are presented in Table III-14 and Figures III-24 to III-27.

#### 4. Methylcyclohexane-Sulfurhexafluoride

The effect of sulfur hexafluoride on the product yields from the radiolysis of MCH vapor was determined in the range from 0 to 10 mole percent SF<sub>6</sub>. The samples containing the SF<sub>6</sub>-MCH mixtures were irradiated in the Gammacell at a 110°C and 375 Torr to a dose of  $4.9 \times 10^{19}$  ev/gram.





TABLE III-14

Yields of Products from MCH-N<sub>2</sub>O Mixtures as a Function of Temperature

Mole % N <sub>2</sub> O	Temp. °C	Press. (Torr)	g				
			H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	Total MC	Total Dimer
9.7 x 10 <sup>-3</sup>	110	377	5.35	0.32	-	2.30	0.33
9.3 x 10 <sup>-3</sup>	160	420	5.48	0.31	-	3.42	0.17
9.8 x 10 <sup>-3</sup>	200	455	5.43	0.40	-	4.45	0.19
0.482	50	124	3.38	8.72	0.64	2.78	0.72
0.435	70	136	3.28	12.5	0.78	7.26	0.99
0.470	110	148	3.24	16.0	1.14	12.8	1.33
0.507	160	168	3.34	15.2	1.38	14.4	1.00
0.467	203	185	3.45	15.1	1.82	14.9	1.97
0.462	255	205	6.34	23.0	10.6	19.7	1.35
6.64	50	124	3.44	21.4	-	11.7	0.75
10.5	50	124	3.08	24.0	-	10.7	0.79
6.61	110	148	3.33	23.2	-	17.0	0.86
1.84	110	152	3.32	21.6	-	15.2	1.71
6.98	110	374	2.96	22.6	-	16.3	1.59
6.53	161	169	3.30	17.7	-	15.2	1.57
3.98	163	169	3.04	18.6	-	14.9	1.29
6.90	201	183	3.56	16.3	-	13.9	1.03

FIGURE III-24

Product Yields from MCH-Nitrous Oxide Mixtures as a Function of  
Temperature

Nitrous oxide concentration = 0.01 mole %

Pressure: 377-455 Torr

A: Hydrogen

B: Nitrogen

C: Total MC

D: Total Dimer

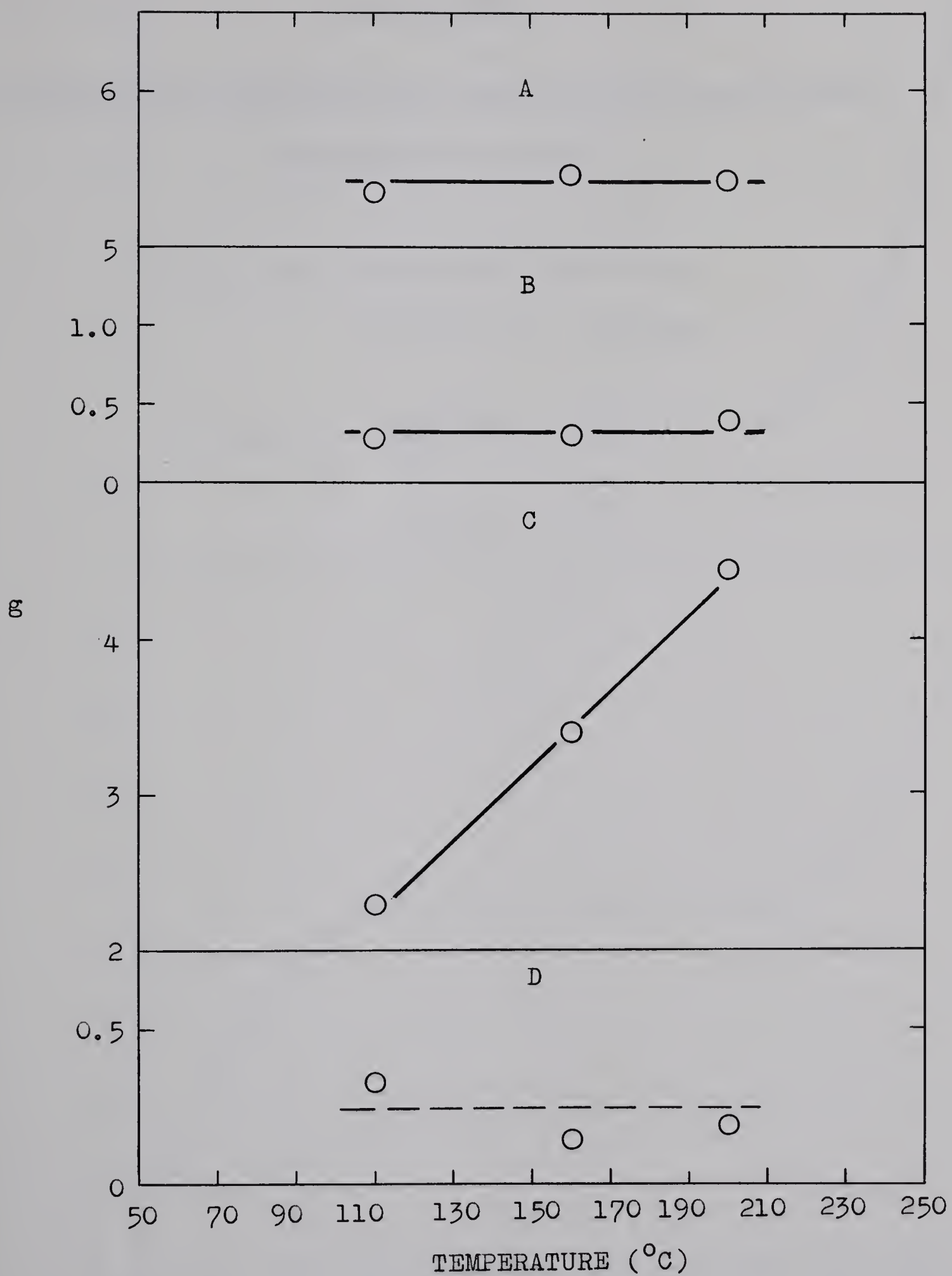


FIGURE III-25

Yields of Hydrogen and Nitrogen from MCH-Nitrous Oxide Mixtures as a  
Function of Temperature

Nitrous oxide concentration = 0.5 mole %

Pressure: 124-205 Torr

A: Hydrogen

B: Nitrogen



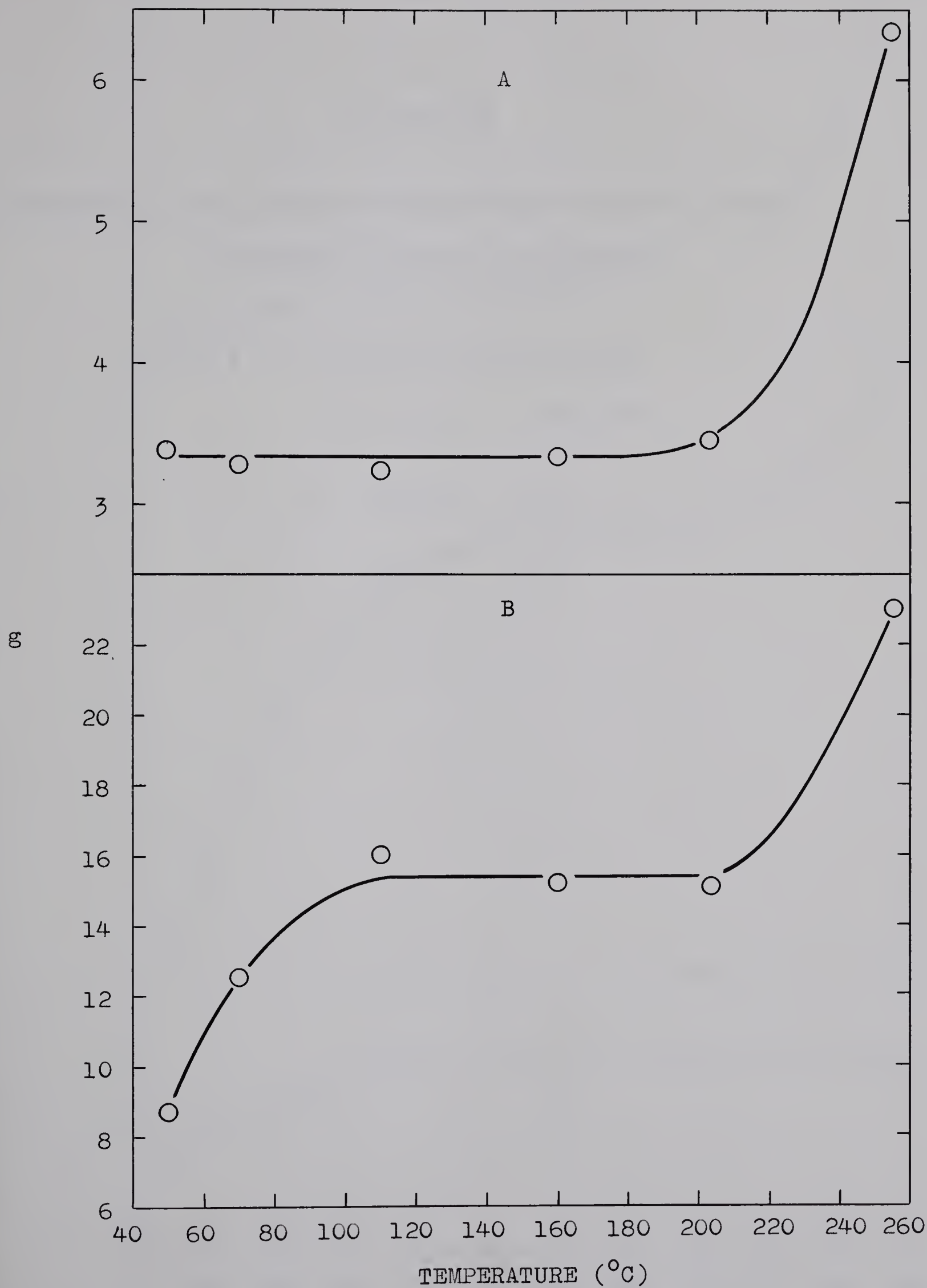


FIGURE III-26

Yields of Methane, Total MC and Total Dimer from MCH-Nitrous Oxide

Mixtures as a Function of Temperature

Nitrous oxide concentration = 0.5 Mole %

Pressure: 124-205 Torr

A: Methane

B: Total MC

C: Total Dimer

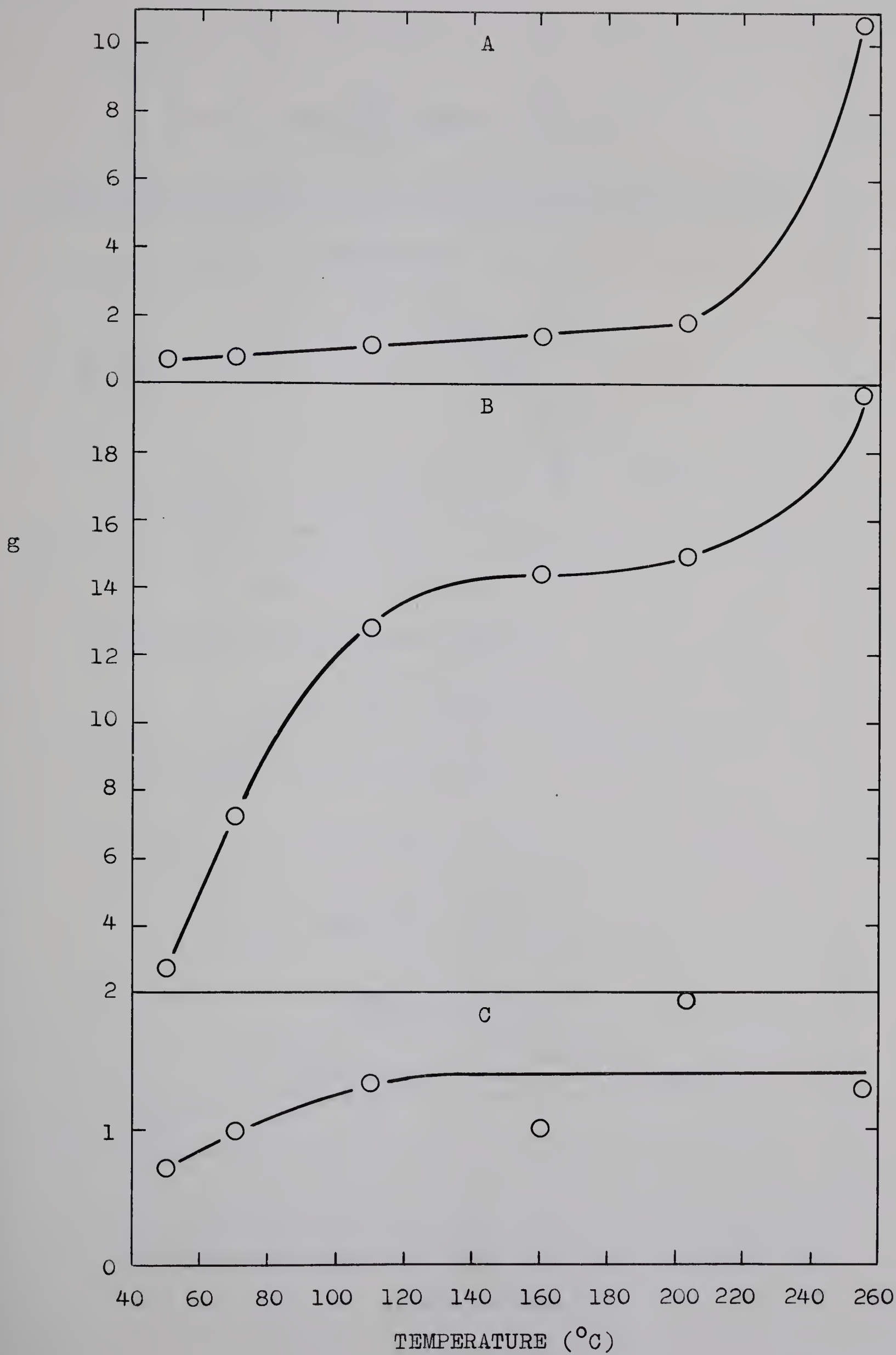


FIGURE III-27

Product Yields from MCH-Nitrous Oxide Mixtures as a Function of  
Temperature

◻: pressure = 124-183 Torr

N<sub>2</sub>O concentration 6.53-6.90 Mole %

◼: pressure = 152 Torr

N<sub>2</sub>O concentration = 1.84 Mole %

△: pressure = 169 Torr

N<sub>2</sub>O concentration = 3.98 Mole %

○: pressure = 374 Torr

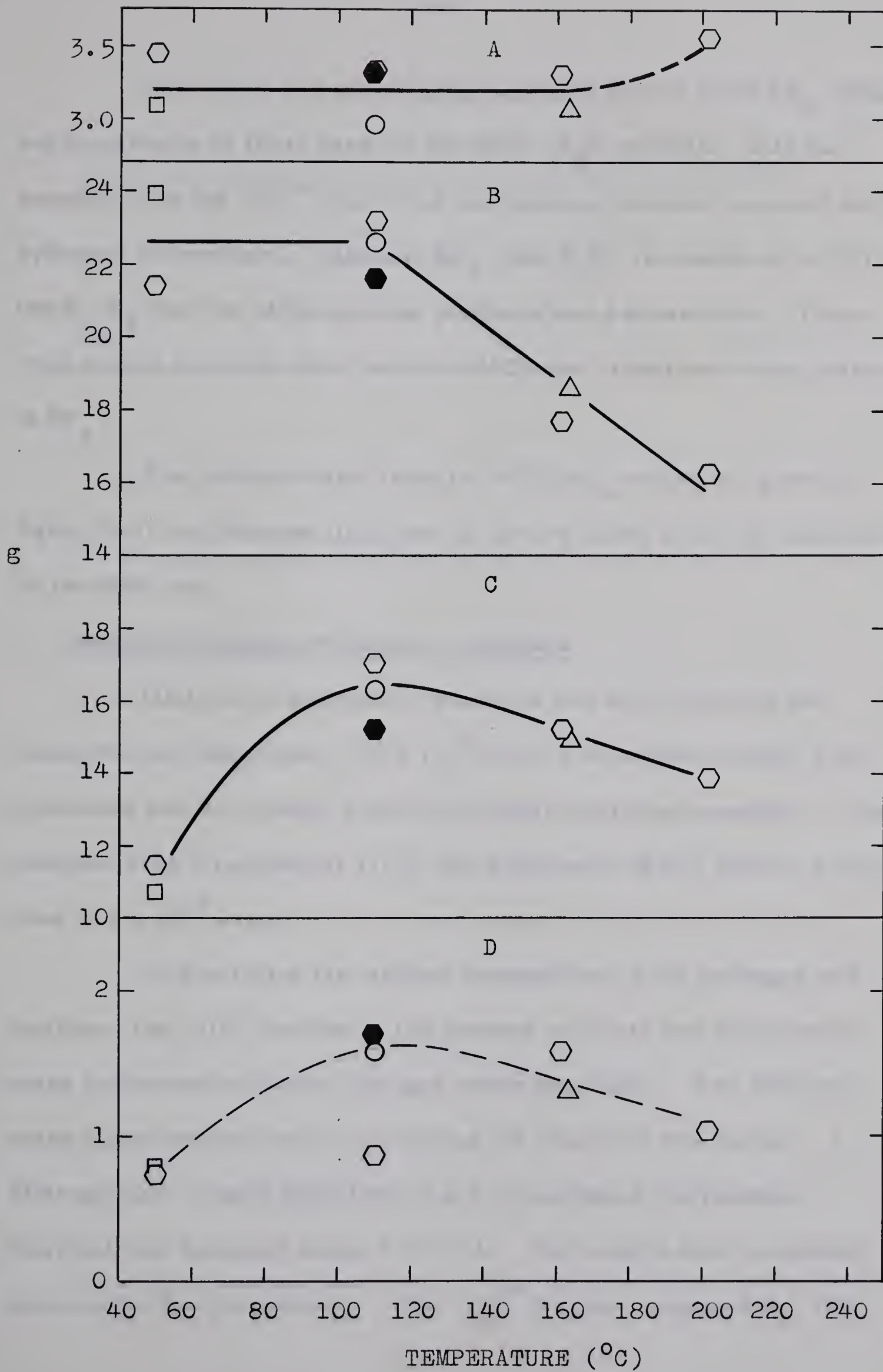
N<sub>2</sub>O concentration = 6.98 Mole %

A: Hydrogen

B: Nitrogen

C: Total MC

D: Total Dimer







The filling and analytical procedures for the MCH-SF<sub>6</sub> system were analogous to those used for the MCH-N<sub>2</sub>O mixtures, with the exception that the -210° fraction of the gaseous products contained only hydrogen and methane. Because SF<sub>6</sub>, like N<sub>2</sub>O, is volatile at -112°C the C<sub>2</sub>-C<sub>4</sub> fraction of the gaseous products was not analysed. There were no new products observed when MCH was irradiated in the presence of SF<sub>6</sub>.

The product yields from the MCH-SF<sub>6</sub> radiolysis given in Table III-15 and Figures III-28 and III-29 are based on energy absorbed by the MCH only.

#### 5. Methylcyclohexane-Perdeutero Ammonia

Mixtures of perdeutero ammonia and MCH covering the concentration range from  $1.02 \times 10^{-2}$  to 10.2 mole percent ND<sub>3</sub> were irradiated and the product yields from these mixtures measured. These samples were irradiated at 110°C and a pressure of 375 Torr to a total dose of  $5 \times 10^{19}$  ev/g.

To determine the isotopic composition of the hydrogen and methane, the -210° fraction of the gaseous products was analysed by mass spectrometry rather than gas chromatography. Two different mass spectrometers were used during the course of this series; a Metropolitan-Vickers Model MS-2 and Consolidated Corporation, Residual Gas Analyser model # 21-614. The results were consistent between the two instruments. The -210° fraction contained H<sub>2</sub>, HD,



TABLE III-15Yields of Products from MCH-Sulfurhexafluoride Mixtures

Mole Percent $\text{SF}_6$	g				
	$\text{H}_2$	$\text{CH}_4$	Unknown $\text{C}_5\text{-C}_6$	Total MC	Total Dimer
0	5.31	1.42	0.68	1.77	0.23
$1.45 \times 10^{-3}$	4.20	1.28	-	-	-
$4.06 \times 10^{-3}$	4.03	1.25	-	-	-
$9.56 \times 10^{-3}$	3.27	1.24	-	-	-
$9.40 \times 10^{-2}$	3.01	1.11	0.62	1.70	0.34
$9.50 \times 10^{-2}$	3.08	1.02	-	-	-
1.07	2.94	1.21	0.81	1.78	0.46
4.77	3.02	1.25	0.65	1.93	0.35
10.1	3.05	1.32	0.61	1.89	0.27

FIGURE III-28

Yields of Hydrogen, Methane and Unknown C<sub>5</sub>-C<sub>6</sub> from MCH-Sulfurhexa-  
fluoride Mixtures

A:      Hydrogen

B:      Methane

C:      Unknown C<sub>5</sub>-C<sub>6</sub>

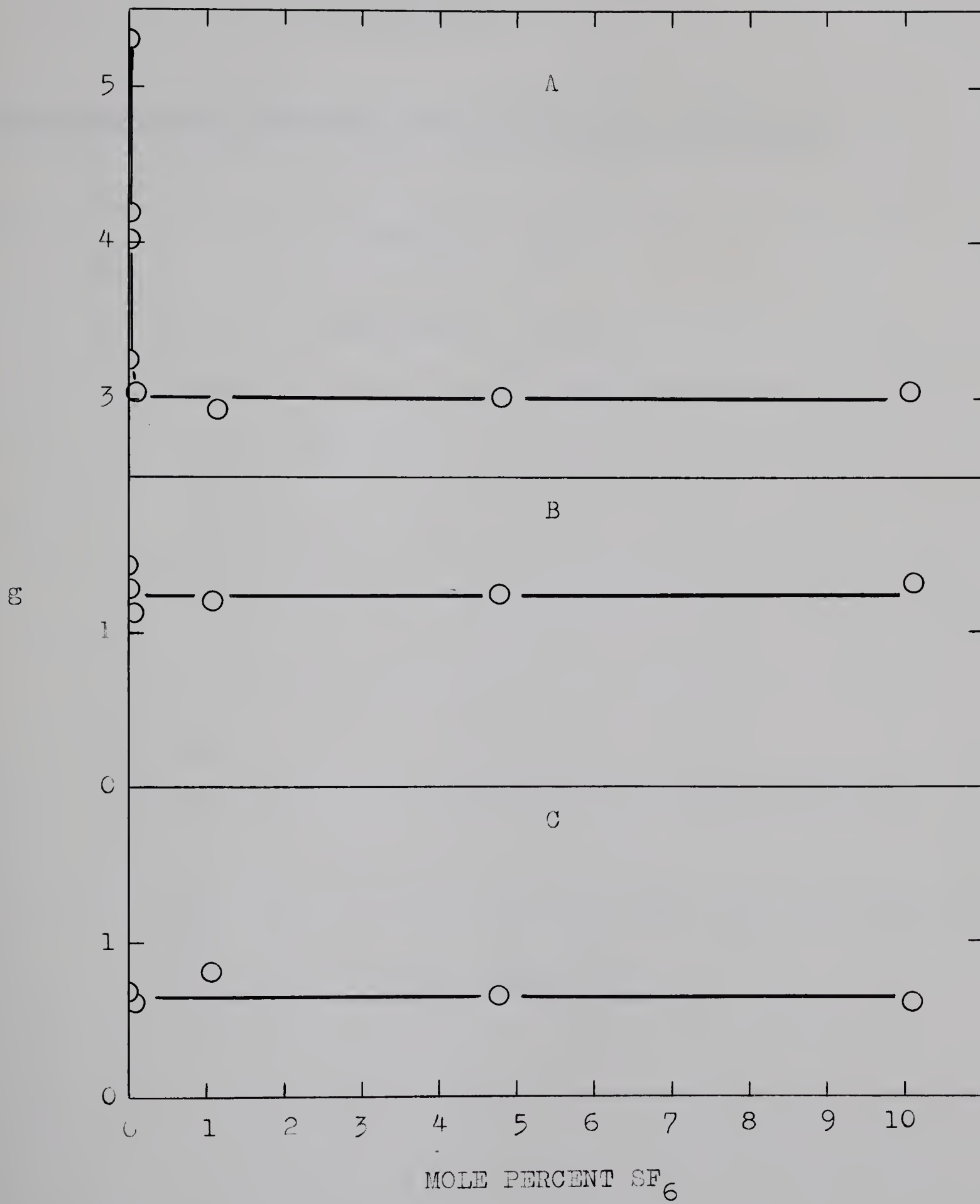


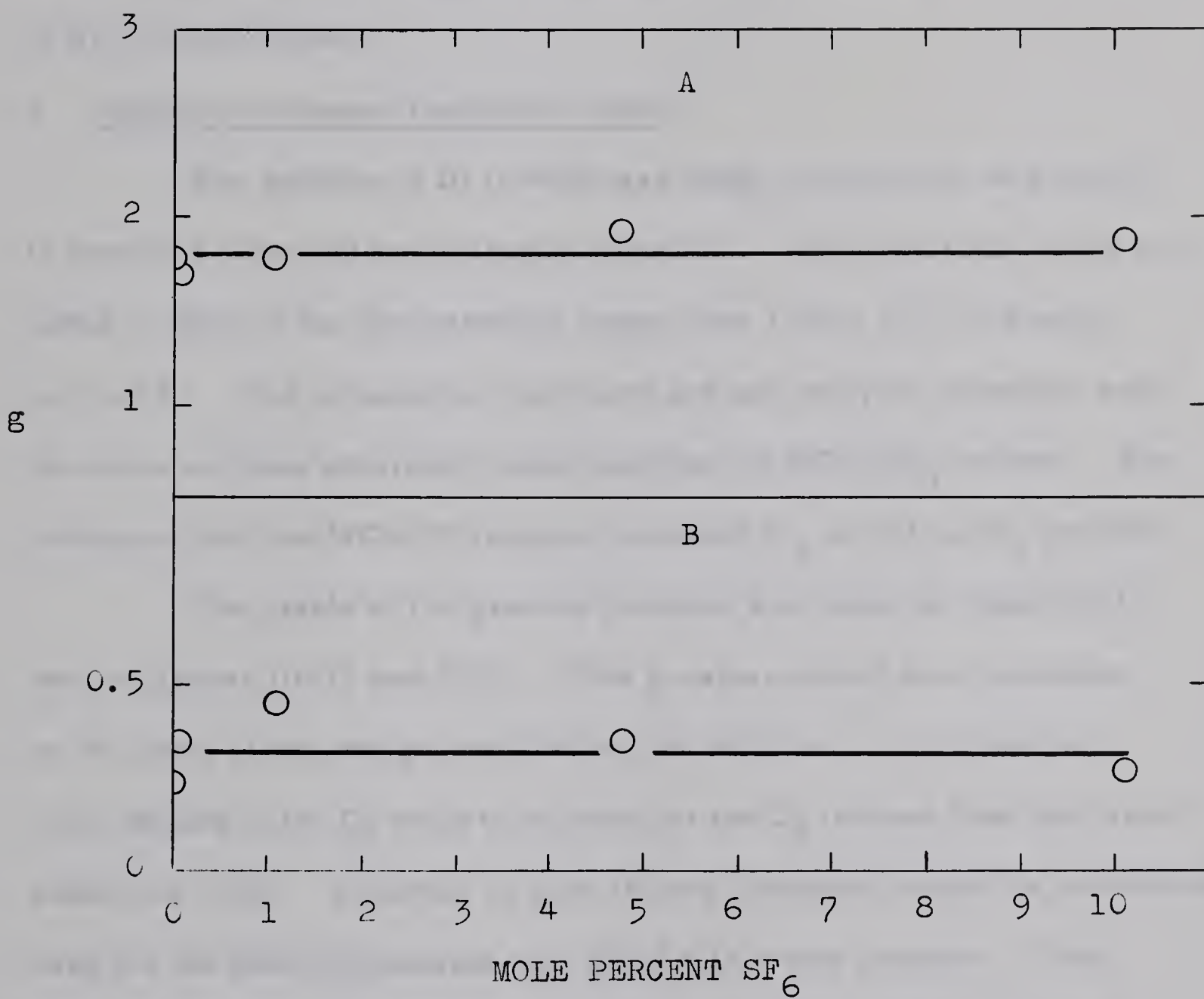
FIGURE III-29

Yield of Total MC and Total Dimer from MCH-Sulfurhexafluoride Mixtures

A: Total MC

B: Total Dimer







$\text{CH}_4$  and  $\text{CH}_3\text{D}$ . Quantitative results were obtained by calibration of the mass spectrometers with authentic samples of these gases.

Figures III-30 and III-31 and Table III-16 present the yields of the main radiolysis products in the  $\text{MCH-ND}_3$  system, as a function of  $\text{ND}_3$  concentration.

#### 6. Methylcyclohexane-Deuterium Iodide

The addition of DI to MCH was made primarily in an attempt to study the nature of the hydrogen formation. The deuterium iodide was added to MCH in the concentration range from  $1.86 \times 10^{-2}$  to 8 mole percent DI. The irradiation conditions and gas analysis technique were the same as those previously mentioned for the  $\text{MCH-ND}_3$  system. The hydrogen from the  $\text{MCH-DI}$  samples contained  $\text{D}_2$  as well as  $\text{H}_2$  and  $\text{HD}$ .

The yields of the gaseous products are shown in Table III-17 and in Figures III-32 and III-33. The g-values quoted are calculated on the basis of the energy absorbed by the MCH only. Corrections were applied to the  $\text{D}_2$  yield to account for the  $\text{D}_2$  formed from the direct radiolysis of DI. A sample of pure DI was irradiated under the conditions used for the  $\text{MCH-DI}$  mixtures, and  $g(\text{D}_2) = 23.4$  was obtained. This yield served as a basis for the correction applied to the  $\text{D}_2$  yield. In addition to the correction for the direct radiolysis of DI a blank correction was necessary. Two blank samples, 1% DI and 10% DI were prepared. These samples were heated to  $110^\circ\text{C}$ , placed in the sample position of the Gammacell and with the timer set at 0.0 minutes, were given a dose

FIGURE III-30Yield of Hydrogens from MCH-Perdeutero Ammonia Mixtures

A: Total Hydrogen

B:  $\text{H}_2$

C: HD

g

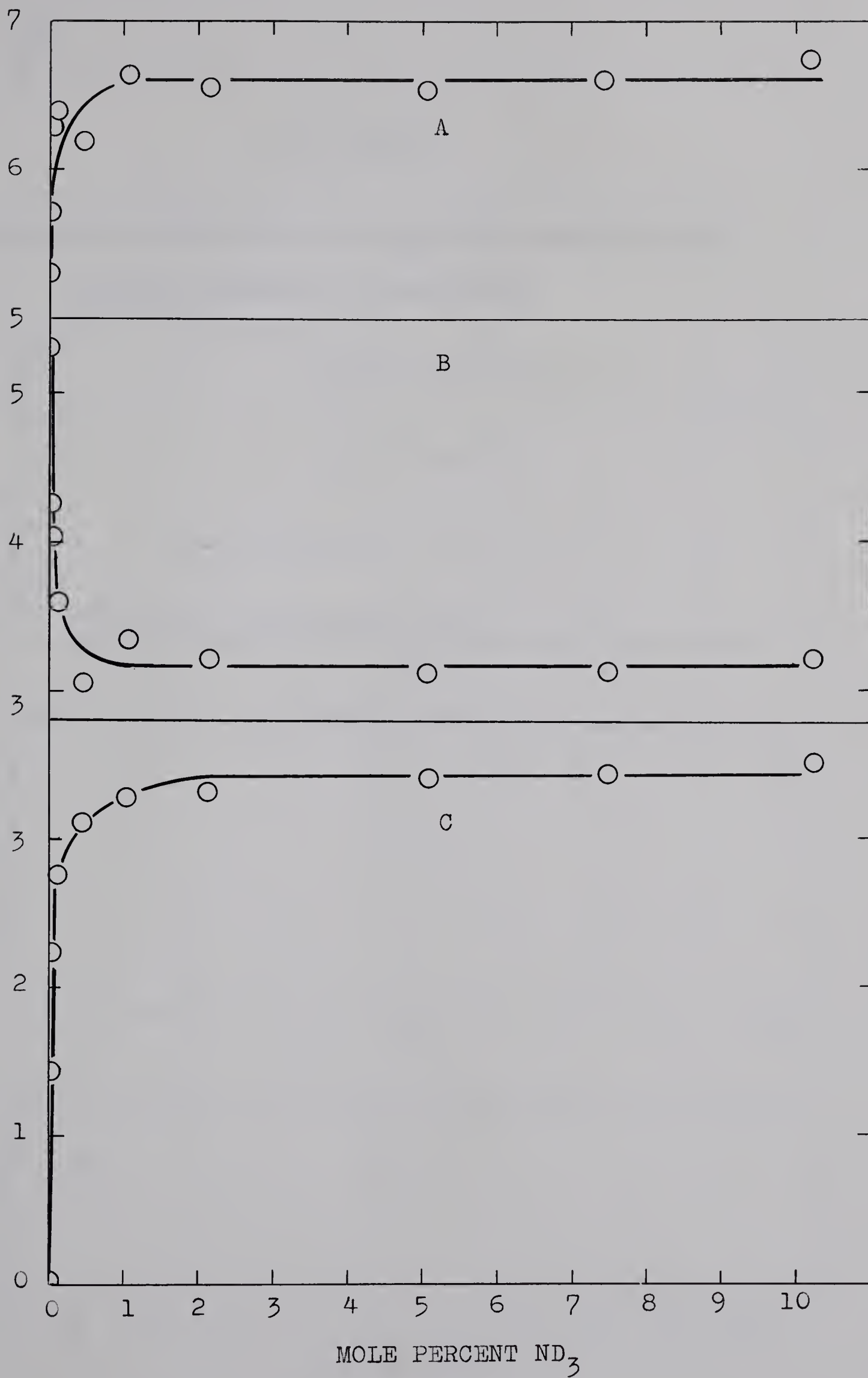


FIGURE III-31

Yield of Methane, Unknown C<sub>5</sub>-C<sub>6</sub>, Total MC and Total Dimer from  
MCH-Perdeutero Ammonia Mixtures

A: CH<sub>4</sub>

B: CH<sub>3</sub>D

C: Unknown C<sub>5</sub>-C<sub>6</sub>

D: Total MC

E: Total C<sub>14</sub>



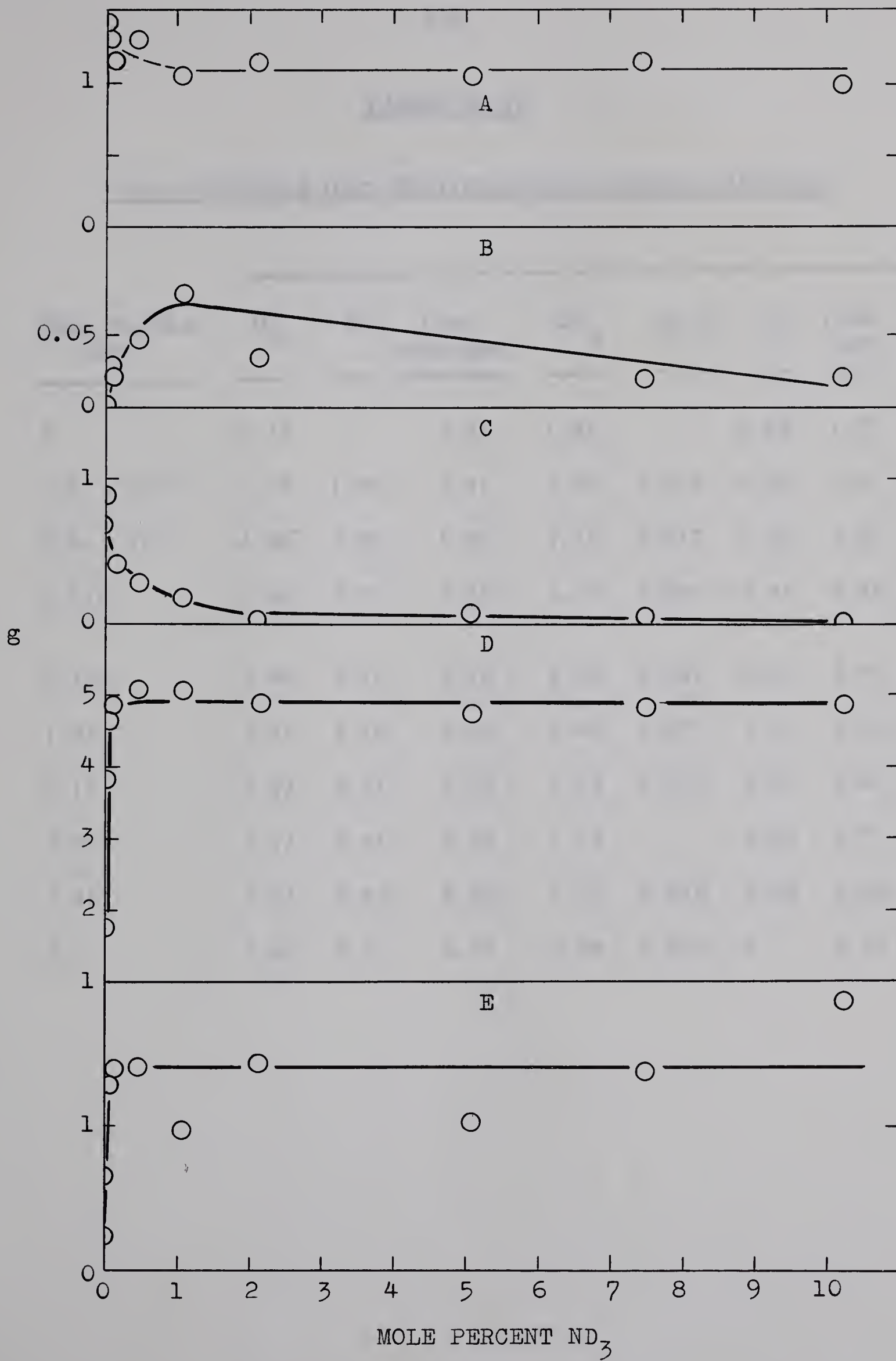




TABLE III-16Yields of Product from MCH-Perdeutero Ammonia Mixtures

Mole Percent ND <sub>3</sub>	g							
	H <sub>2</sub>	HD	Total Hydrogen	CH <sub>4</sub>	CH <sub>3</sub> D	C <sub>6</sub>	Total MC	Total Dimer
0	5.31	-	5.31	1.42	-	0.68	1.77	0.23
1.02 x 10 <sup>-2</sup>	4.27	1.44	5.71	1.09	0.025	0.90	3.83	0.64
5.81 x 10 <sup>-2</sup>	4.05	2.24	6.29	1.30	0.027	0.55	4.62	1.28
0.110	3.62	2.76	6.38	1.15	0.020	0.41	4.88	1.35
0.467	3.06	3.12	6.18	1.30	0.047	0.27	5.05	1.42
1.03	3.36	3.28	6.64	1.06	0.077	0.16	5.08	0.95
2.11	3.22	3.33	6.55	1.15	0.033	0.03	4.89	1.43
5.05	3.12	3.41	6.53	1.15	-	0.08	4.73	1.01
7.45	3.14	3.44	6.58	1.16	0.018	0.08	4.80	1.37
10.2	3.22	3.51	6.73	0.98	0.022	0	4.85	1.88



TABLE III-17Yields of Products from MCH-DI System

Mole Percent DI	g								
	H <sub>2</sub>	HD	D <sub>2</sub>	Total Hydrogen	CH <sub>4</sub>	CH <sub>3</sub> D	Unk. C <sub>5</sub> -C <sub>6</sub>	Total MC	Total Dimer
0	5.31	-	-	5.31	1.42	-	0.60	1.77	0.23
1.86 x 10 <sup>-2</sup>	4.43	1.02	0	5.45	0.33	0.13	0.74	1.87	0.08
0.293	2.84	2.59	0.38	5.77	0.12	0.20	0.83	1.31	0
0.642	2.03	2.70	1.16	5.79	0.17	0.57	0.94	1.23	0
1.19	1.53	2.75	1.80	6.08	0.23	0.80	0.83	1.26	<u>U.P.A.</u> 0.07
1.32	1.77	2.66	1.80	6.23	0.19	0.83	0.64	1.10	0.08
2.62	1.89	2.64	2.18	6.71	0.17	0.61	0.85	1.13	0.22
3.92	1.60	2.45	2.34	6.39	0.11	0.56	0.55	0.80	0.30
7.94	1.58	2.51	2.32	6.43	0.18	1.03	0.71	0.71	0.30

FIGURE III-32Yield of Hydrogens from MCH-Deuterium Iodide Mixtures

A: Total Hydrogen

B:  $H_2$

C: HD

D:  $D_2$



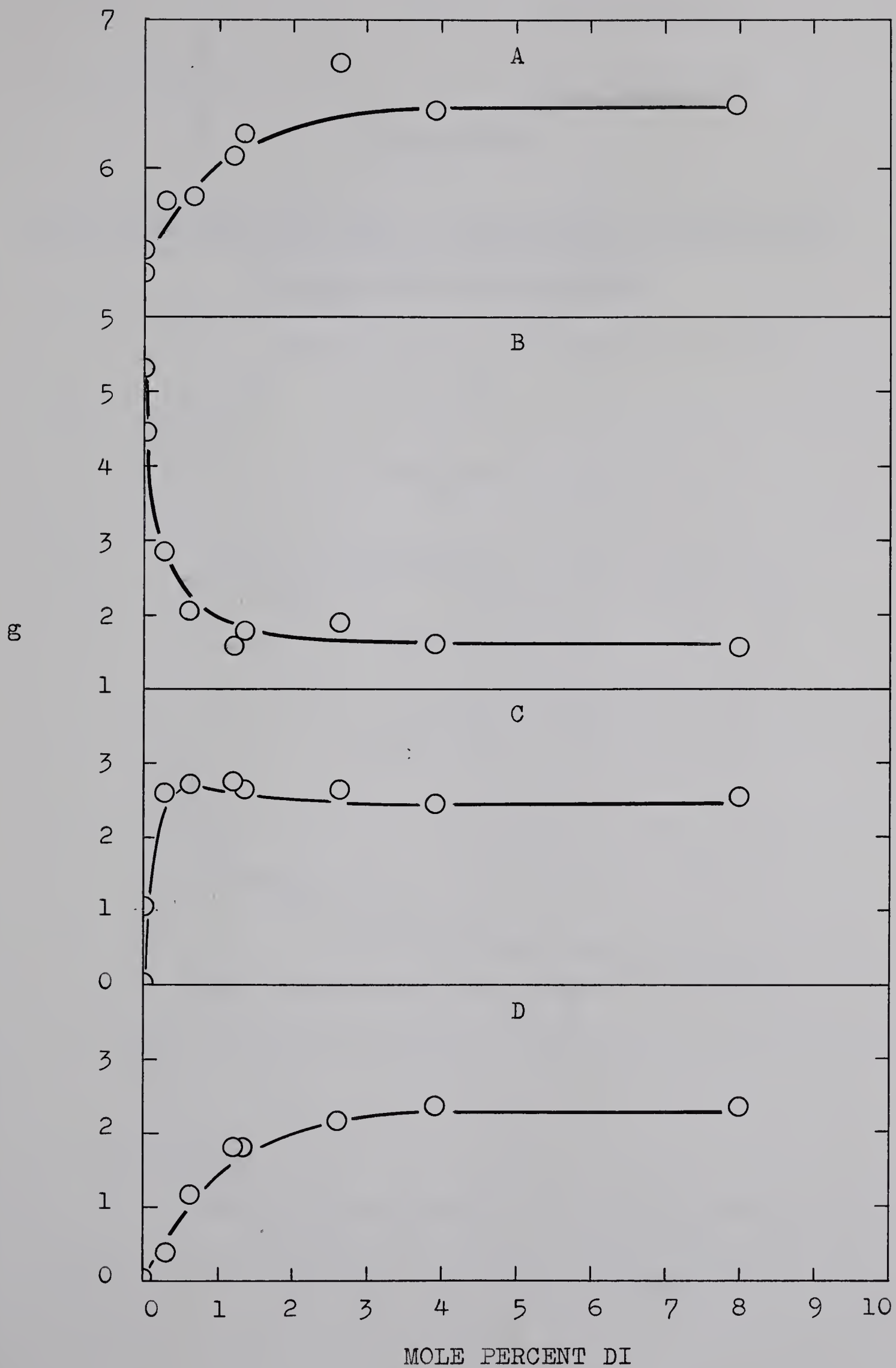


FIGURE III-33

Yield of Methane, Unknown C<sub>5</sub>-C<sub>6</sub>, Total MC, Total Dimer from  
MCH-Deuterium Iodide Mixtures

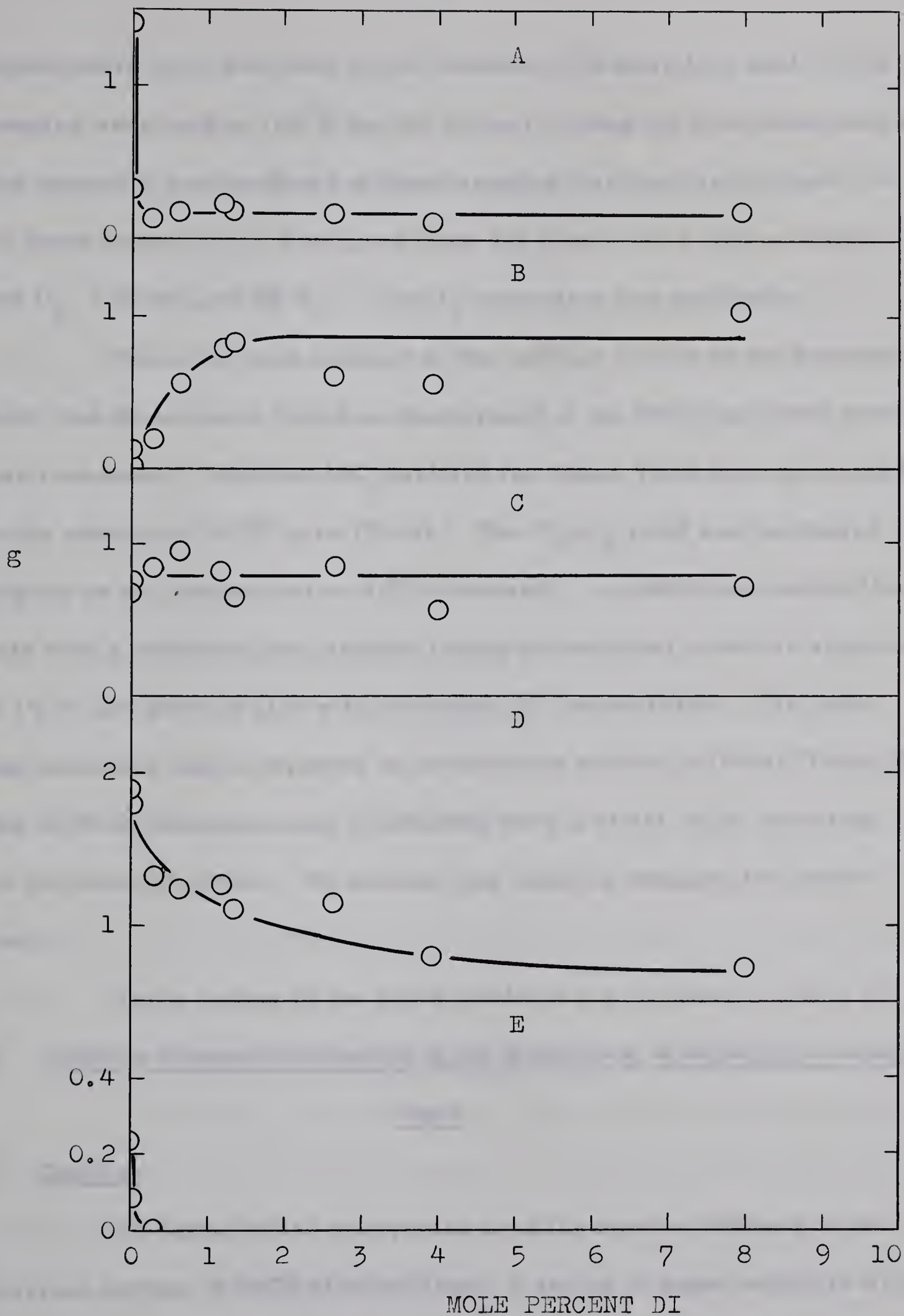
A: CH<sub>4</sub>

B: CH<sub>3</sub>D

C: Unknown C<sub>5</sub>-C<sub>6</sub>

D: Total MC

E: Total C<sub>14</sub>





equivalent to the travel time of the Gammacell drawer ( $\sim 4$  sec). The samples were held at  $110^{\circ}\text{C}$  for the normal irradiation time when analysed. The amount of gas produced in these samples was used as the basis for the blank correction. The gases from the blanks were approximately 85%  $\text{D}_2$ , 12% HD and 3%  $\text{H}_2$ . The  $\text{H}_2$  correction was negligible.

While the main interest in the addition of DI was the hydrogen yield, the three major liquid products found in the MCH radiolysis were also measured. Both the MC yield and the dimer yield were decreased by the addition of DI (Figure III-33). The  $\text{C}_5\text{-C}_6$  yield was increased slightly as the concentration of DI increased. An additional unidentified peak with a retention time similar to that of the dimer products appeared at 1% DI and grew in size with increased DI concentration. Its yield was estimated and is reported as unidentified product A (UPA) (Table III-17). The MCH-DI solutions after irradiation were a violet color indicating the presence of iodine. No attempt was made to measure the iodine yield.

The g-values of the liquid products are included in Table III-17.

#### E. Additive Competition Studies in the Radiolysis of Methylcyclohexane

##### Vapor

##### 1. General

To assist in the interpretation of the results obtained in the previous section of MCH plus additives, a series of experiments in which two additives were allowed to compete with each other in the MCH system





were performed. These experiments were designed specifically to obtain information on the hydrogen yield. In some cases however liquid products were also measured. These particular cases are mentioned in the appropriate section below.

The conditions and techniques used in all the competition studies were the same, and similar to those previously described for the MCH additive systems of section D. All irradiations were carried out in the Gammacell at  $110^{\circ}\text{C}$  to a total dose of  $5 \times 10^{19}$  ev/g. All g values quoted are calculated on the basis of energy absorbed by MCH only. The pressure of MCH in the samples was 375 Torr.

## 2. Deuterium Iodide-Ethylene in Methylcyclohexane

The competition between DI and  $\text{C}_2\text{H}_4$  in MCH was studied at two fixed concentrations of DI; 1.1% and 4.9%. For each of these DI-MCH compositions,  $\text{C}_2\text{H}_4$  was added to cover the range from 1% to 17% in the case of the 1.1% DI solution, and to 20% in the case of the 4.9% DI solution. The product yields are presented in Figure III-34 and Table III-18.

## 3. Deuterium Iodide-Sulfurhexafluoride in Methylcyclohexane

The DI- $\text{SF}_6$  competition was studied under similar conditions of concentration as the DI- $\text{C}_2\text{H}_4$  study, i.e. approximately 1% and 5% solutions of DI in MCH, with various amounts of added  $\text{SF}_6$ . In this series of experiments the  $\text{SF}_6$  covered the concentration range from approximately 0.1 mole % to 10 mole %. The product yields are

FIGURE III-34Yields of Hydrogens from MCH-Deuterium Iodide-Ethylene Mixtures

○: 1% DI

△: 5% DI

A: Total Hydrogen

B:  $H_2$

C: HD

D:  $D_2$

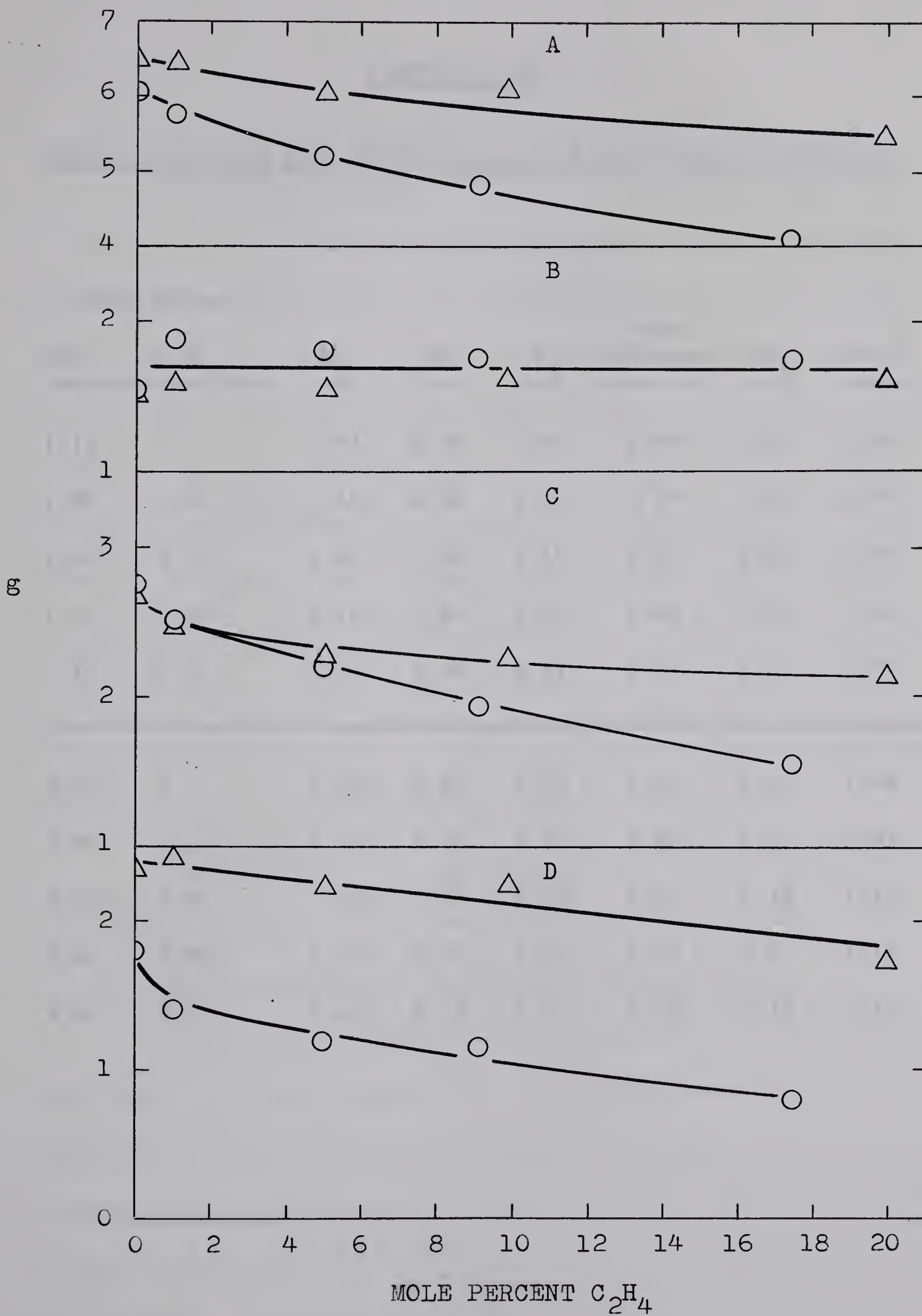




TABLE III-18

Yields of Products from MCH-Deuterium Iodide-Ethylene Mixtures

g							
Mole Percent							
<u>DI</u>	<u>C<sub>2</sub>H<sub>4</sub></u>	<u>H<sub>2</sub></u>	<u>HD</u>	<u>D<sub>2</sub></u>	<u>Total Hydrogen</u>	<u>CH<sub>4</sub></u>	<u>CH<sub>3</sub>D</u>
1.19	0	1.53	2.75	1.80	6.08	0.23	0.80
1.09	1.02	1.88	2.50	1.41	5.79	0.22	0.79
1.08	4.98	1.82	2.20	1.19	5.21	0.20	0.86
1.07	9.08	1.76	1.93	1.15	4.84	0.19	0.83
1.19	17.4	1.75	1.54	0.81	4.10	0.23	0.97
5.08	0	1.50	2.66	2.33	6.49	0.22	1.04
4.94	1.01	1.59	2.46	2.41	6.46	0.17	0.91
4.87	5.01	1.55	2.26	2.22	6.03	0.18	1.11
4.82	9.82	1.61	2.26	2.24	6.11	0.21	1.14
4.87	19.9	1.62	2.12	1.71	5.45	0.18	1.15





summarized in Table III-19 and in Figures III-35.

#### 4. Deuterium Iodide-Nitrous Oxide in Methylcyclohexane

The addition of up to 10%  $N_2O$  to a 1% solution of DI in MCH resulted in no variation of any of the hydrogen or methane yields (see Figure III-36). Furthermore, the large nitrogen yield ( $\sim 22$  g-units) found in solutions of MCH- $N_2O$  was completely suppressed. In an attempt to find the relative concentration of  $N_2O$  and DI at which competition did occur, the concentration of  $N_2O$  was fixed at 1.9% and the amount of DI reduced until the formation of nitrogen was again observed. The first trace of  $N_2$  appeared at a concentration of  $1.2 \times 10^{-2}$  mole % DI in the 1.9 mole %  $N_2O$ -MCH solution (Figure III-37). At this DI concentration the  $D_2$  yield was less than 0.005 g units, while  $G_{HD}$  had decreased to 0.45 and  $G_{H_2}$  had increased to 4.2. All of the measured product yields with differing amounts of DI and  $N_2O$  are presented in Table III-20.

The MC and dimer  $C_{14}$  products were also measured in these  $N_2O$ -DI-MCH mixtures. (See Table III-20 and Figure III-38).

#### 5. Nitrous Oxide-Sulfurhexafluoride in Methylcyclohexane

It was reported in the MCH- $N_2O$  system (Section D3) that a large yield of nitrogen was produced. Johnson and Warman (29) have reported that the  $N_2$  yield from the radiolysis of propane-nitrous oxide mixtures could be eliminated by the addition of  $SF_6$ . Starting with equal amounts of  $N_2O$  and  $SF_6$  (1.9 mole %) in MCH, the same effect was found in this system. The value of  $g(N_2)$  was reduced from 21 in the absence of



TABLE III-19

Yields of Products from MCH-Deuterium Iodide-Sulfurhexafluoride Mixtures

		g					
Mole Percent		H <sub>2</sub>	HD	D <sub>2</sub>	Total Hydrogen	CH <sub>4</sub>	CH <sub>3</sub> D
DI	SF <sub>6</sub>						
1.32	0	1.77	2.66	1.80	6.23	0.19	0.83
1.30	$9.40 \times 10^{-2}$	1.70	2.56	2.10	6.36	0.13	0.71
1.24	0.33	1.69	2.25	1.40	5.34	0.15	0.80
1.23	1.26	1.67	1.68	0.64	3.99	0.16	0.66
1.19	4.74	1.61	1.22	0.19	3.02	0.16	0.54
1.10	9.65	1.66	0.99	0.046	2.70	0.15	0.64
5.08	0	1.50	2.66	2.33	6.49	0.22	1.04
5.13	1.09	1.54	2.42	2.22	6.18	0.15	0.92
5.30	5.46	1.56	2.14	1.20	4.90	0.18	1.05
5.36	10.7	1.63	2.04	0.65	4.32	0.23	1.02

FIGURE III-35Yields of Hydrogens from MCH-Deuterium Iodide-SulfurhexafluorideMixtures

○: 1 Mole % DI

△: 5 Mole % DI

A: Total Hydrogen

B: H<sub>2</sub>

C: HD

D: D<sub>2</sub>

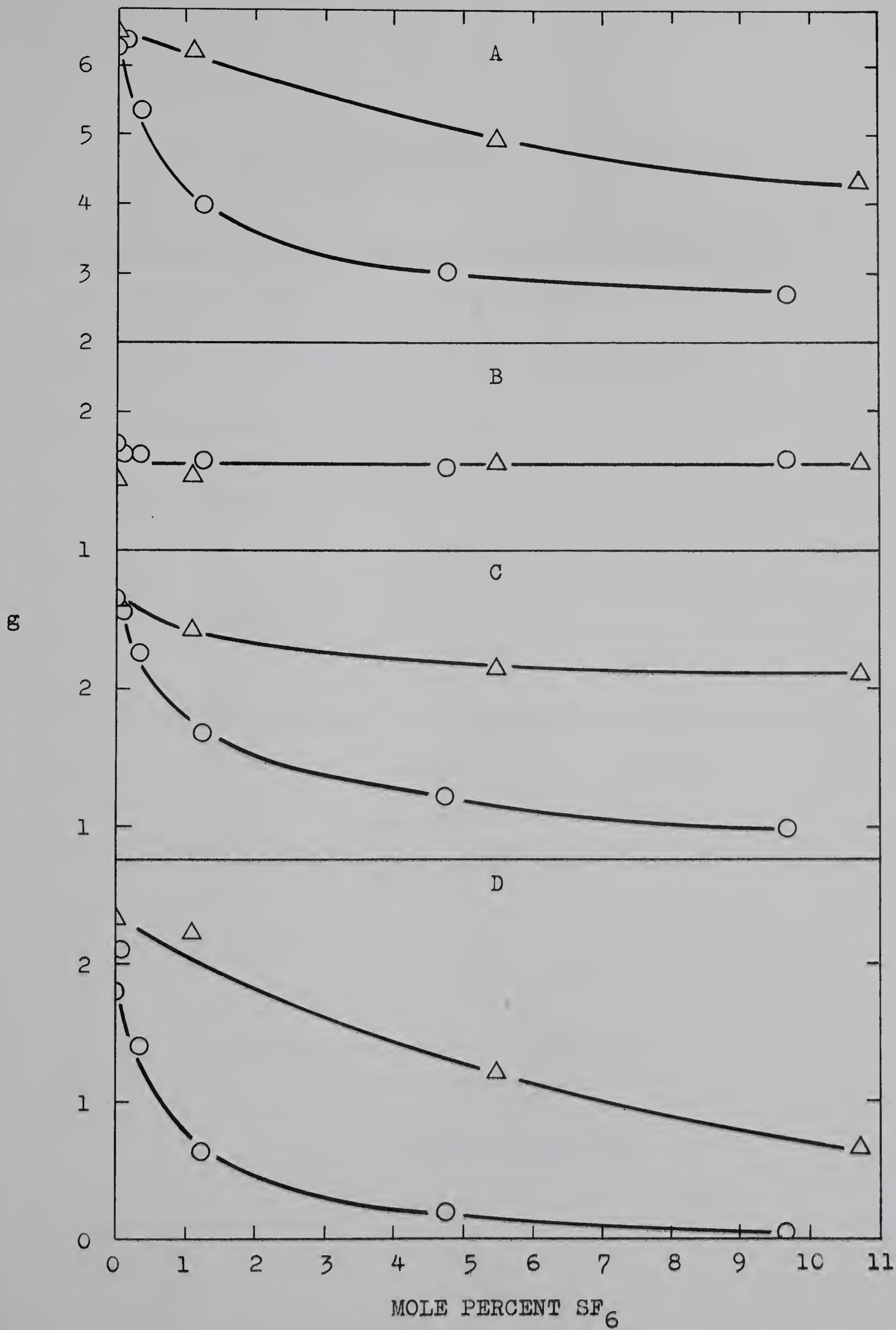


FIGURE III-36Product Yields from MCH-Deuterium Iodide-Nitrous Oxide Mixtures

Constant Deuterium Iodide Concentration = 1 Mole %

A: Total Hydrogen

B:  $\text{H}_2$

C: HD

D:  $\text{D}_2$

E: Methane

○:  $\text{CH}_3\text{D}$

△:  $\text{CH}_4$



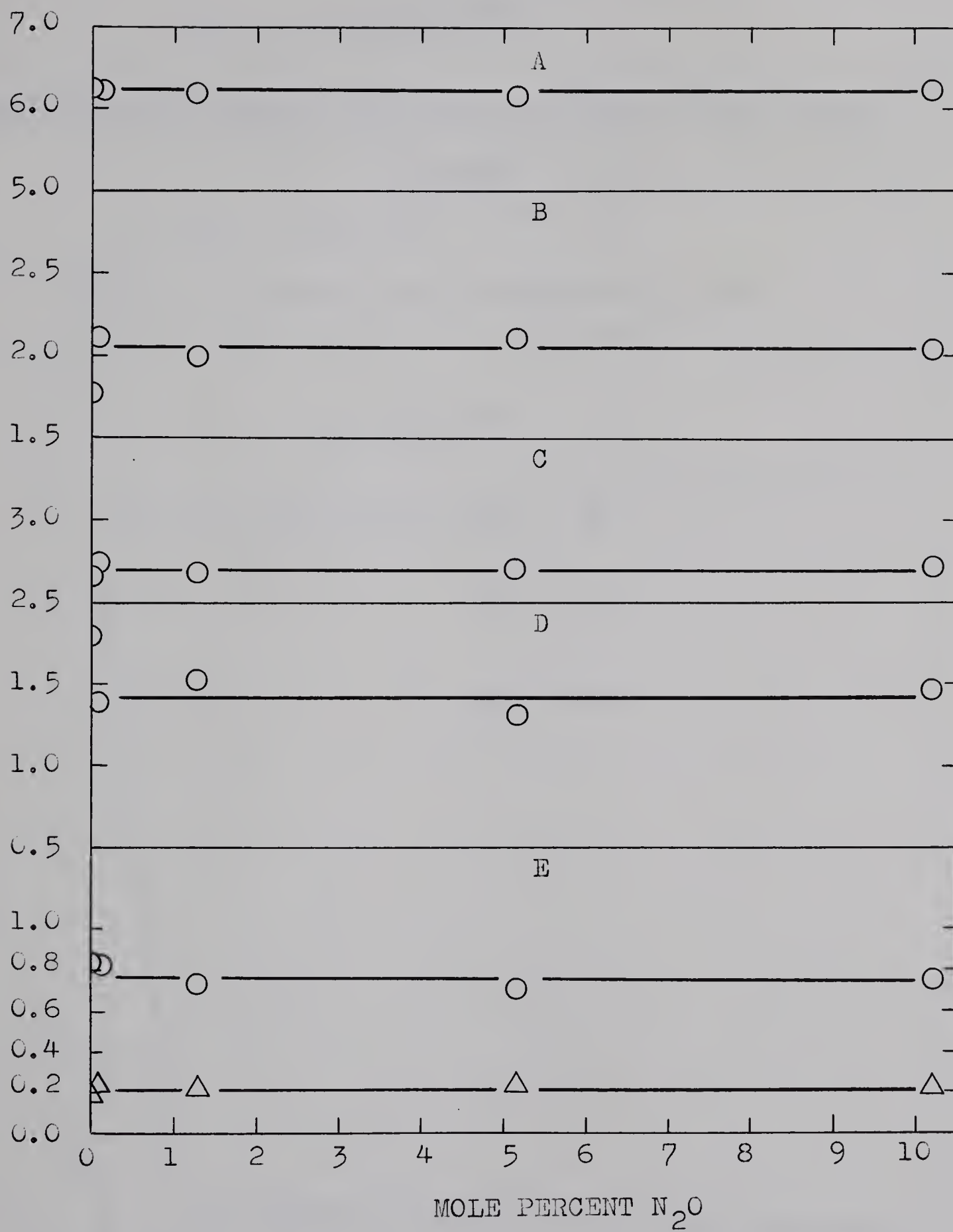


FIGURE III-37Gaseous Product Yields from MCH-Nitrous Oxide-Deuterium Iodide  
Mixtures

Constant Nitrous Oxide Concentration = 2 mole %

A: Total Hydrogen

B:  $\text{H}_2$

C: HD

D:  $\text{N}_2$

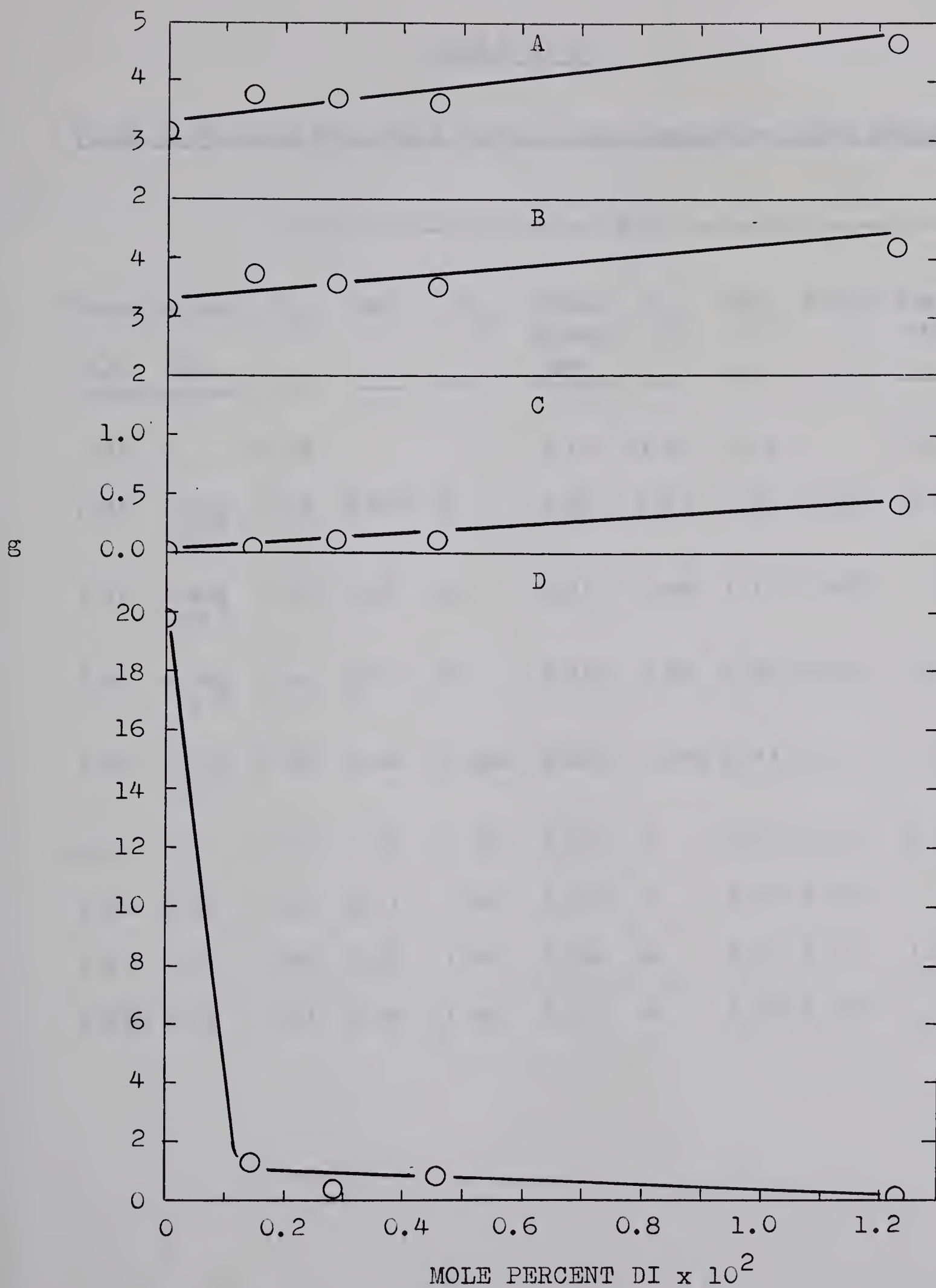




TABLE III-20Yields of Products from MCH-Nitrous Oxide-Deuterium Iodide Mixtures

		g								
Mole Percent <u>N<sub>2</sub>O</u>	<u>DI</u>	<u>H<sub>2</sub></u>	<u>HD</u>	<u>D<sub>2</sub></u>	<u>Total Hydro- gen</u>	<u>N<sub>2</sub></u>	<u>CH<sub>4</sub></u>	<u>CH<sub>3</sub>D</u>	<u>Total MC</u>	<u>Total C<sub>14</sub></u>
1.91	0	3.14	-	-	3.14	19.8	1.34	-	16.0	1.38
1.95	1.45x 10 <sup>-3</sup>	3.74	0.057	0	3.80	1.27	1.02	0.021	2.62	0.14
1.91	2.81x 10 <sup>-3</sup>	3.59	0.12	0	3.71	0.40	1.17	0.065	1.82	0.037
1.95	4.58x 10 <sup>-3</sup>	3.54	0.12	0	3.66	0.86	0.84	0.051	2.10	0.071
1.86	1.23x 10 <sup>-2</sup>	4.22	0.44	0.004	4.66	0.044	0.93	0.14	1.83	0.055
10.2	1.13	2.03	2.72	1.47	6.22	0	0.21	0.77	1.33	0.022
5.14	1.22	2.10	2.71	1.36	6.17	0	0.22	0.69	-	-
1.27	1.25	1.99	2.67	1.52	6.18	0	0.21	0.73	1.52	0.18
0.094	1.21	2.11	2.73	1.38	6.23	0	0.24	0.82	1.20	0.18

FIGURE III-38

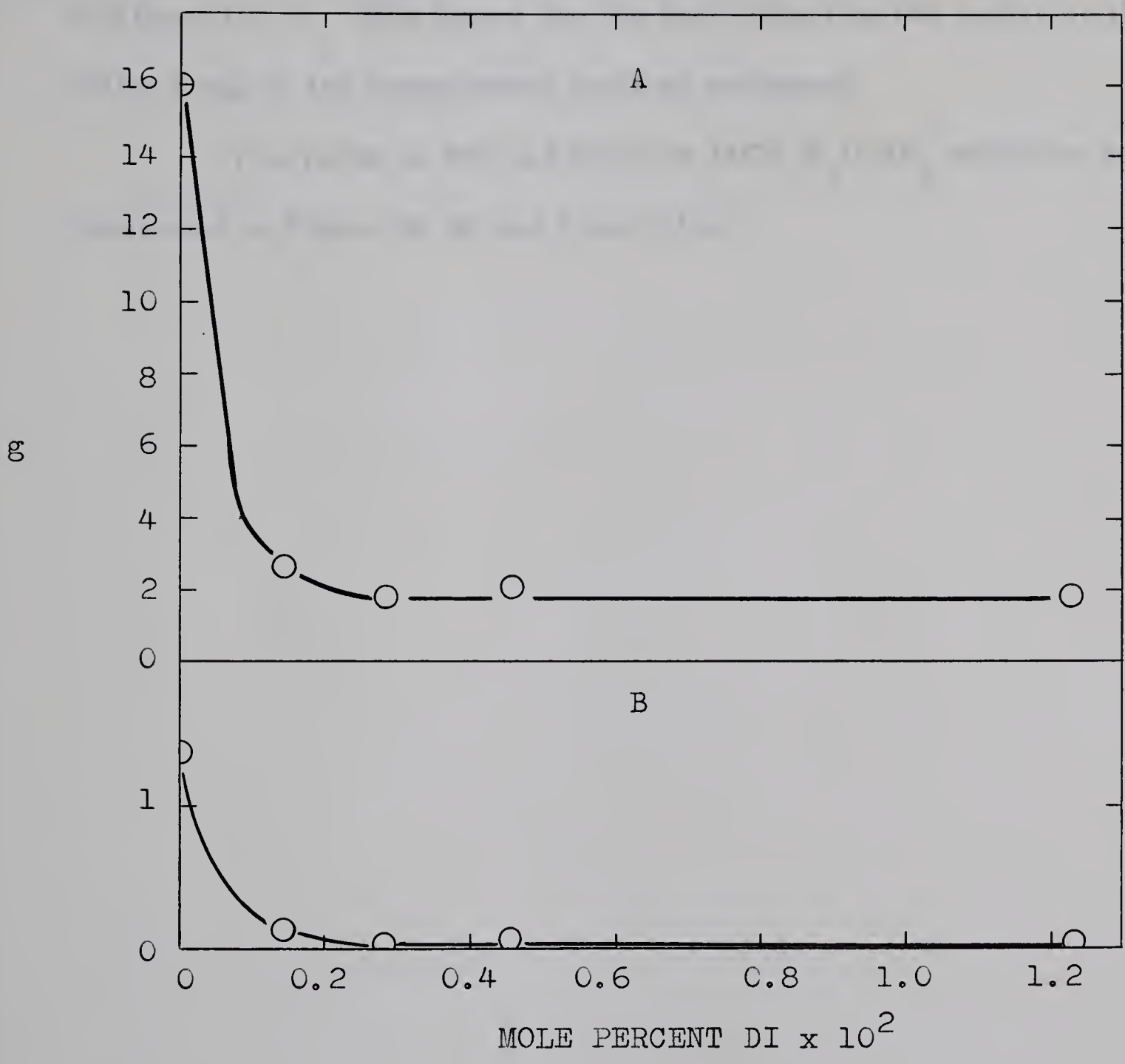
Liquid Product Yields from MCH-Nitrous Oxide-Deuterium Iodide Mixtures

Constant Nitrous Oxide Concentration = 2 Mole %

A: Total MC

B: Total Dimer







$\text{SF}_6$  to less than 0.01 in its presence. The  $\text{N}_2\text{O}$  concentration was then held constant at 1.9% and the amount of  $\text{SF}_6$  decreased until  $\text{N}_2$  was again formed. The results of this competition between  $\text{N}_2\text{O}$  and  $\text{SF}_6$  is shown in Figure III-39. This figure has the data plotted on two scales so the entire range of the experiments could be presented.

The yields of MC and dimer in  $\text{MCH-N}_2\text{O-SF}_6$  mixtures are illustrated in Figure III-40 and Table III-21.

FIGURE III-39

Yield of Hydrogen and Nitrogen from MCH-Nitrous Oxide-Sulfurhexafluoride

Mixtures

Constant Nitrous Oxide Concentration = 2 Mole %

○: Top Scale

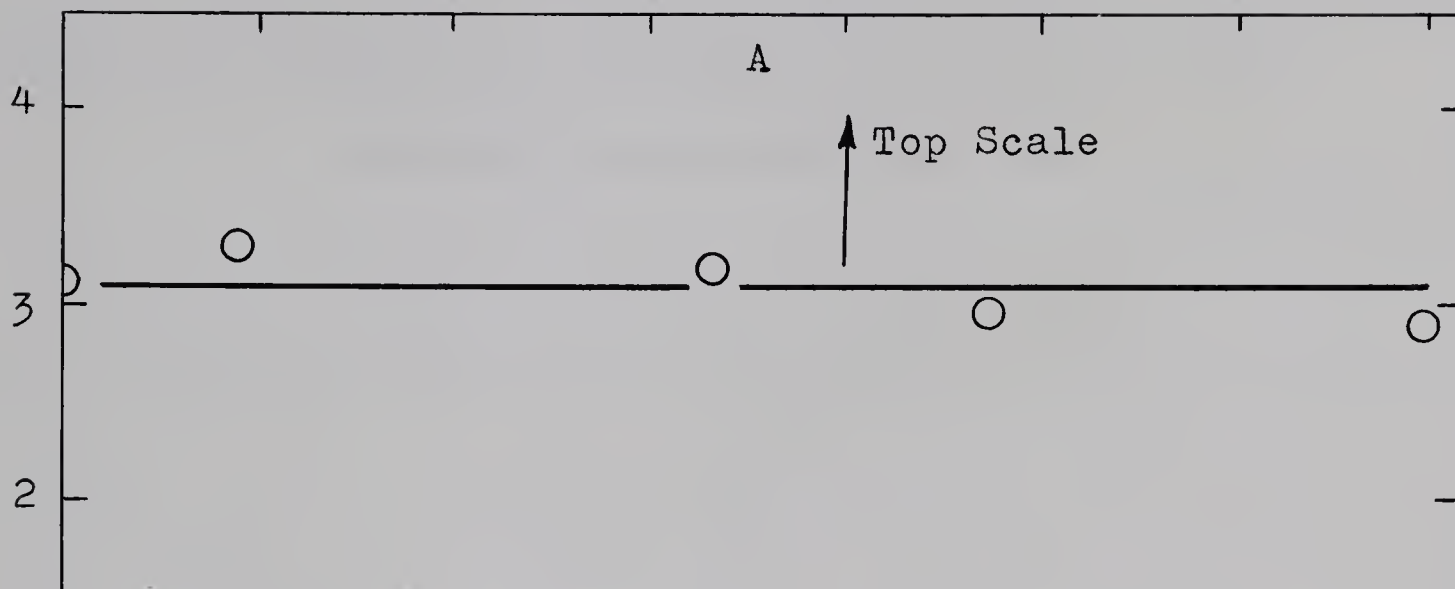
△: Bottom Scale

A: Hydrogen

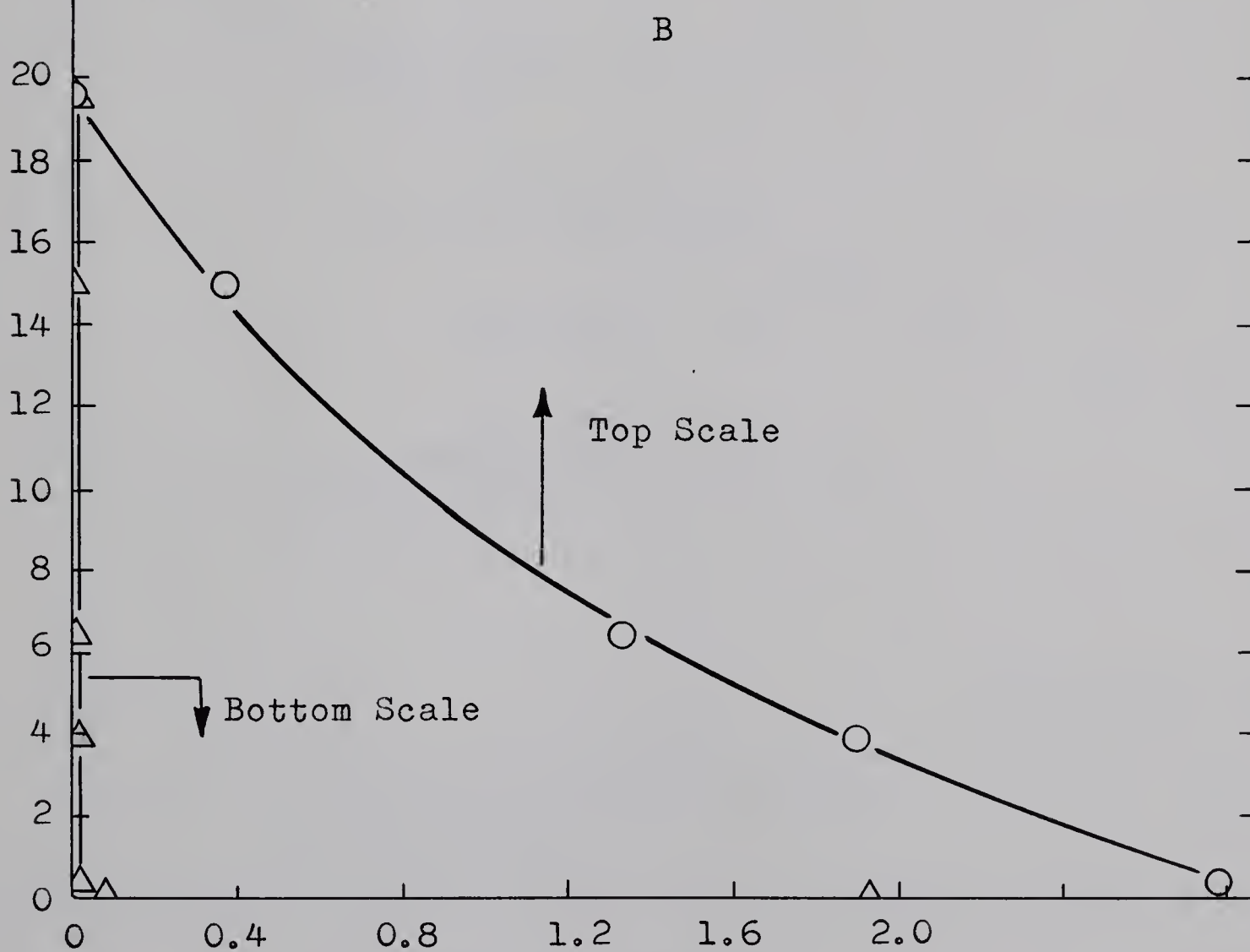
B: Nitrogen

MOLE PERCENT  $\text{SF}_6 \times 10^2$

0 0.2 0.4 0.6 0.8 1.0 1.2 1.4



g



MOLE PERCENT  $\text{SF}_6$

FIGURE III-40

Yield of Unknown C<sub>5</sub>-C<sub>6</sub>, Total MC, Total Dimer from MCH-Nitrous  
Oxide-Sulfurhexafluoride Mixtures

Constant Nitrous Oxide Concentration = 2 Mole %

○: Top Scale

△: Bottom Scale

A: Unknown C<sub>5</sub>-C<sub>6</sub>

B: Total MC

C: Total Dimer



MOLE PERCENT  $\text{SF}_6 \times 10^2$

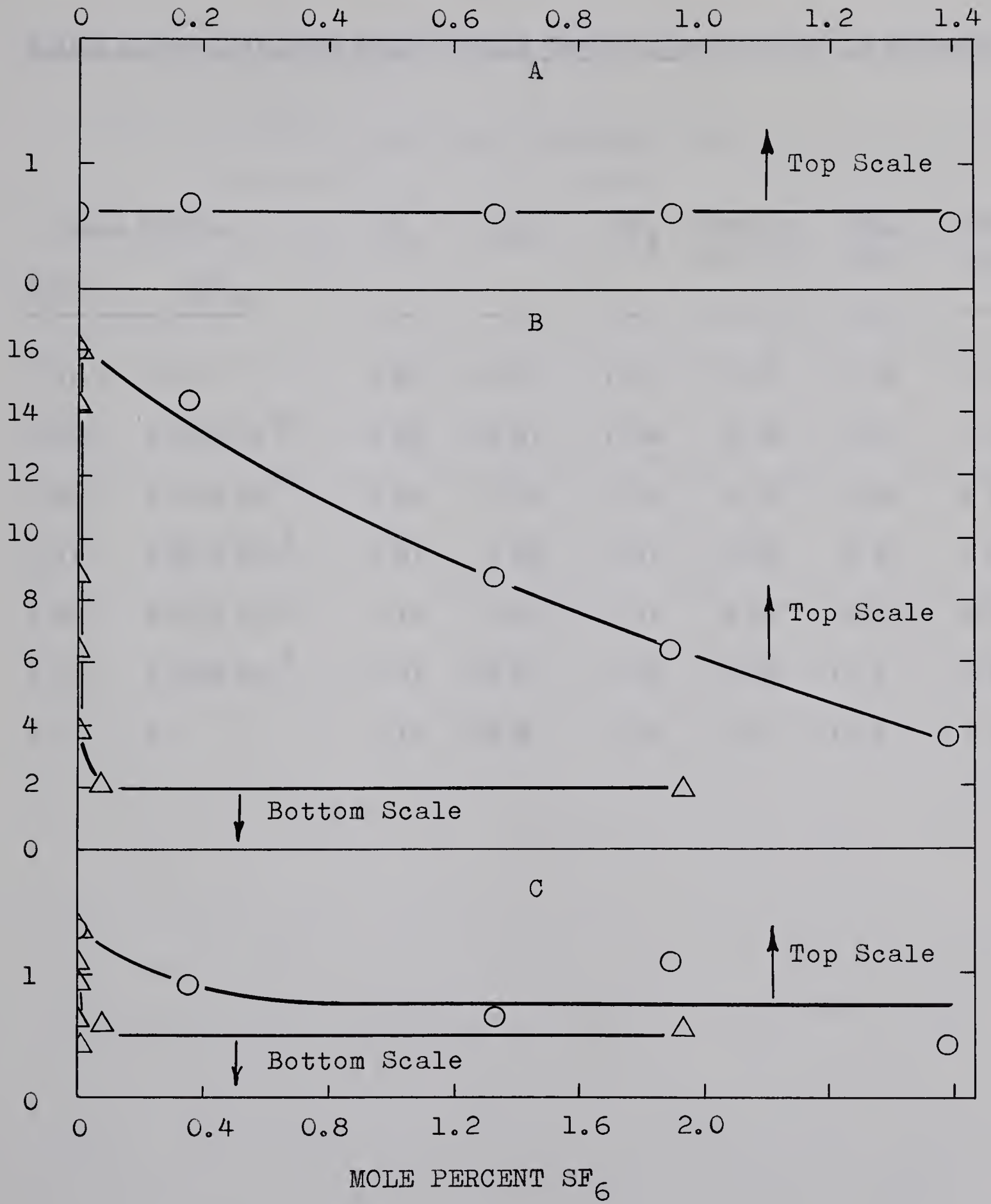




TABLE III-21

Yields of Products from MCH-Nitrous Oxide-Sulfurhexafluoride Mixtures

		g					
Mole Percent		H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	Unknown C <sub>5</sub> -C <sub>6</sub>	Total MC	Total C <sub>14</sub>
<u>N<sub>2</sub>O</u>	<u>SF<sub>6</sub></u>						
1.94	1.93	2.93	<0.01	1.25	0.35	1.98	0.55
1.88	7.80 x 10 <sup>-2</sup>	2.92	<0.01	1.24	0.34	2.07	0.59
1.83	1.39 x 10 <sup>-2</sup>	2.90	0.38	1.38	0.54	3.80	0.41
1.91	9.43 x 10 <sup>-3</sup>	2.97	3.98	1.21	0.62	6.42	1.09
1.92	6.61 x 10 <sup>-3</sup>	3.19	6.42	1.35	0.61	8.76	0.63
1.87	1.78 x 10 <sup>-3</sup>	3.31	15.0	1.32	0.68	14.4	0.91
1.91	0	3.14	19.8	1.34	0.61	16.0	1.38



## DISCUSSION

A. Pure Methylcyclohexane1. Material Balance

The material balance for the radiolysis products from MCH vapor is given in Table IV-1. As is shown in this material balance, there are approximately 5 G-units of hydrogen deficient products that have not been detected. Similar poor material balances have also been observed in other gas phase radiolysis studies of alkanes. In the  $\gamma$ -radiolysis of cyclohexane, Blachford and Dyne (61) reported a shortage of 7 G-units of hydrogen deficient products and Theard (21) found that approximately 5 G-units of hydrogen deficient products were not detected. In the  $\alpha$ -particle radiolysis of cyclohexane vapor (81) a similar deficiency of 7 G-units was found. In cyclohexane, this material imbalance was attributed to the formation of polymer products which were not measured by the analytical techniques used. Ramaradhya and Freeman (81) have suggested that this polymerization reaction may be an ionic process. Because of the similarity of the cyclohexane system to the present study of MCH, an analogous polymerization reaction is suggested to account for the non-detected hydrogen deficient products. In the high dose samples, a non-volatile residue remained in the bottom of the cell after the MCH plus liquid products were distilled out. While this residue was not measured, its presence constitutes evidence that a polymer was formed.





TABLE IV-1

Material Balance for Pure MCH

<u>Product</u>	<u>G<sub>i</sub></u>	<u>H<sub>2</sub> Equivalent*</u>
H <sub>2</sub>	5.22	+5.22
CH <sub>4</sub>	1.34	+1.34
C <sub>2</sub> H <sub>4</sub>	1.46	0.00
C <sub>3</sub> H <sub>6</sub>	0.78	0.00
C <sub>2</sub> H <sub>2</sub>	0.27	-0.27
C <sub>2</sub> H <sub>6</sub>	0.34	+ 0.34
C <sub>3</sub> H <sub>8</sub>	0.21	+ 0.21
C <sub>4</sub> H <sub>10</sub>	0.19	+ 0.19
Unknown C <sub>5</sub> -C <sub>6</sub> (Assume C <sub>5</sub> H <sub>10</sub> )	0.90	0.00
Total MC	1.95	-1.95
Total Dimer	0.28	-0.28
		<hr/>
Total =		+ 4.80

\* The hydrogen equivalent of a product corresponds to the amount of hydrogen in that product in excess of the empirical formula (CH<sub>2</sub>)<sub>n</sub>.

MCH is (CH<sub>2</sub>)<sub>7</sub>.



## 2. Gaseous Products

### a. Hydrogen

The hydrogen yield was independent of dose over the range from  $0.3$  to  $18 \times 10^{19}$  ev/g (see Figure III-5). This dose independence was also observed for the total hydrogen plus methane yield ( $G(-196^{\circ}\text{C})$ ) in the  $\alpha$ -particle radiolysis of MCH by Ramaradhya. A similar lack of dose dependence of the hydrogen yield from cyclohexane vapor has been observed by Theard (21) in the  $\gamma$ -radiolysis and by Ramaradhya and Freeman in the  $\alpha$ -radiolysis (81). Blachford and Dyne (61) found that  $G(\text{H}_2)$  from cyclohexane decreased from 5.44 to 4.93 over the dose range  $3.5$  to  $7.0 \times 10^{19}$  eV/g.

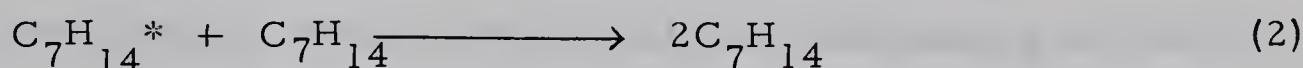
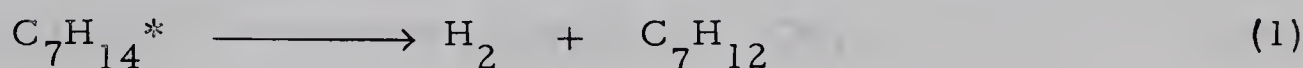
The value of  $G(\text{H}_2)$  was independent of temperature from  $60^{\circ}\text{C}$  to about  $200^{\circ}\text{C}$  where the yield started to increase with further increase in temperature; at  $260^{\circ}$ ,  $G(\text{H}_2)$  had risen to 6.3 (Figure III-12). A similar behavior of the hydrogen yield with temperature was previously observed in a temperature study done with cyclohexane vapor (61). In cyclohexane the increase seems to start at a slightly higher temperature, although because of the scatter of the experimental points in both studies, it is difficult to define the exact temperature at which the yield start to rise. The larger hydrogen yields at high temperatures is probably due to radiation induced pyrolysis (61).

A change in pressure from 37 to 610 Torr at  $110^{\circ}\text{C}$  had no effect on  $G(\text{H}_2)$  (Figure III-9). If there were competing gas phase and



wall reactions for the precursors of hydrogen, then as the pressure was lowered the reaction at the wall should be favored because of faster diffusion of the precursor to the wall. The lack of a pressure effect indicates that either the product yields from the wall reactions and gas phase reactions were the same or that wall reactions are not significant in the formation of hydrogen in this system.

A pressure effect on the hydrogen yield would be expected if the following competition occurred in the system.



The absence of a pressure effect on  $G(\text{H}_2)$  indicates that if reaction (1) is a source of hydrogen its lifetime is less than  $10^{-10}$  sec; based on the collision frequency of a gas at 610 Torr and assuming reaction (2) occurs with unit efficiency. In the radiolysis of ethane (98) a pressure effect on  $G(\text{H}_2)$  was observed only at pressures above 75 atmospheres.

#### b. Methane

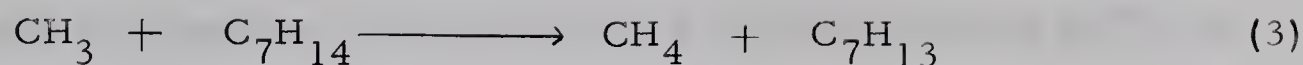
The decomposition of MCH to yield methane was greater in the  $\gamma$ -radiolysis ( $G = 1.34$ ) than in the  $\alpha$ -radiolysis ( $G \approx 0.2$ ) (80). A similar higher methane yield was observed between the  $\gamma$ - and  $\alpha$ -radiolysis of cyclohexane vapor (61, 81). The high yield of methane from MCH is not unexpected, because of the methyl group present in MCH. Methyl radicals are known to abstract a hydrogen atom from alkanes (99) so one



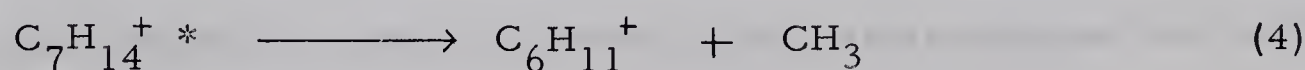




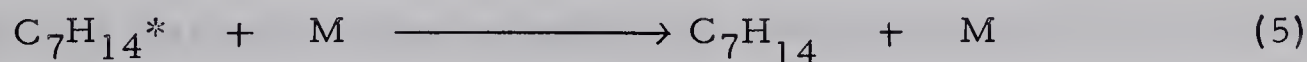
source of methane is probably



The reduction of the methane yields by free radical scavengers such as  $\text{C}_2\text{H}_4$  and DI (discussed in Section B) indicates that reaction (3) is a major source of methane. Methyl radicals could result from the decomposition of an excited MCH molecule or the fragmentation of the parent ion. Since  $\text{C}_6\text{H}_{11}^+$  is the largest ion in the mass spectrum of MCH a likely source of methyl radicals is the fragmentation reaction.



The increase of the methane yield with decreasing pressure (Figure III-11) supports the suggestion that methyl radicals are formed by unimolecular decomposition processes. An estimate of the lifetime of the excited molecule or ion can be calculated from the observed pressure effect, if unit efficiency is assumed for the reaction competing with decomposition.



$\text{C}_7\text{H}_{14}^*$  can be an ion or an excited molecule. From the collision frequency of a molecule at the lowest pressure studied, the lifetime of the excited species is at least  $10^{-9}$  sec.

The increase of the methane yield with increasing temperature indicates the existence of an effective competition for either the methyl radicals or the precursors of the methyl radical. A competition between reactions such as (4) and (5) was shown by the pressure effect. If these



reactions have different activation energies then the competition would be temperature sensitive. The rapid rise of  $G(\text{CH}_4)$  above  $200^\circ\text{C}$  is probably due to radiation induced pyrolysis of MCH as suggested previously for hydrogen.

#### c. $\text{C}_2$ , $\text{C}_3$ and $\text{C}_4$ Products

The principal products in this fraction were ethane, ethylene, propane and propylene. Normal and iso-butane were also present, but because of the difficulty in estimating the butane yield (see the experimental section), full confidence cannot be placed in the values obtained and so they will not be discussed. Because the sensitivity of the analytical equipment to acetylene was low, measurement of its yield was uncertain. The G-value for acetylene was measured only in the dose study.

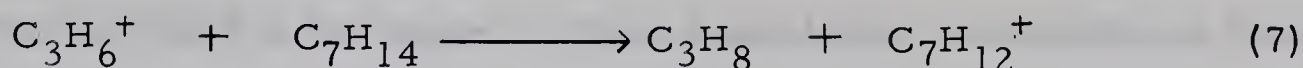
The product yields in the  $\text{C}_2$ - $\text{C}_4$  fraction were all independent of dose over the range studied (Figures III-6 and III-7). The propane yield was not dependent on either temperature or pressure, while the yield of ethane was independent of pressure, but increased with increasing temperature. Both  $G(\text{C}_2\text{H}_4)$  and  $G(\text{C}_3\text{H}_6)$  increased with increasing temperature and with decreasing pressure. This difference of behavior indicates the formation of saturated and unsaturated gases with the same carbon number is from different precursors. It is therefore unlikely that the  $\text{C}_2$  and  $\text{C}_3$  products arise from the disproportionation reactions of ethyl and propyl radicals.

There are a number of ion molecule reactions which can explain

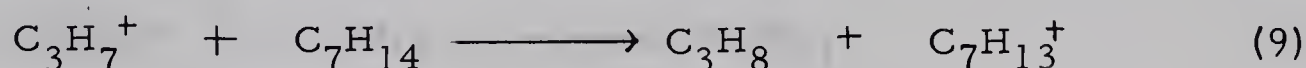
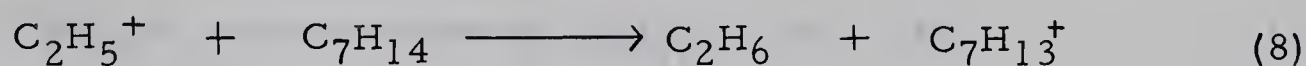




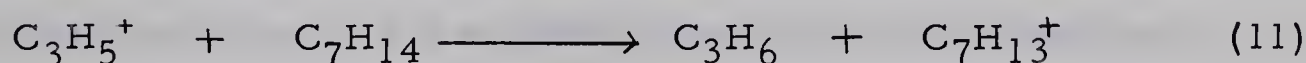
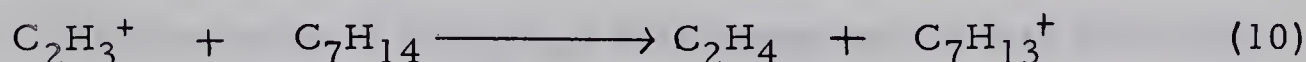
the formation of these gaseous products. Ethane and propane can be formed in the  $\text{H}_2^-$  transfer reactions.



The  $\text{H}_2^-$  transfer reaction to an olefin ion from a saturated hydrocarbon has been demonstrated by Doepker and Ausloos (73). Hydride ion transfer reactions such as



may also contribute to the formation of these products (74). Hydride ion transfer reactions to the ions  $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_5^+$ , which are observed in the mass spectrum of MCH, are possible sources of ethylene and propylene.



The pressure effect on the yields of ethylene and propylene indicates that the precursors of  $\text{C}_2\text{H}_3^+$  and  $\text{C}_3\text{H}_5^+$  had a lifetime  $> 10^{-9}$  sec, whereas the absence of pressure effect on  $G(\text{C}_2\text{H}_6)$  and  $G(\text{C}_3\text{H}_8)$  suggests that formation of the  $\text{C}_2\text{H}_4^+$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{C}_3\text{H}_6^+$  and  $\text{C}_3\text{H}_7^+$  ions occurred in  $10^{-9}$  sec. (Assuming unit efficiency for the reaction competing with the fragmentation reaction).

### 3. Liquid Products

#### a. Methylcyclohexene (MC)

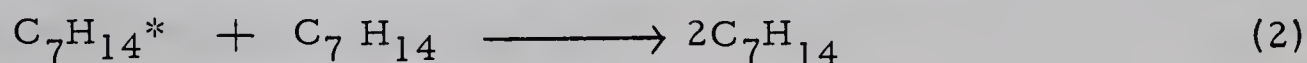
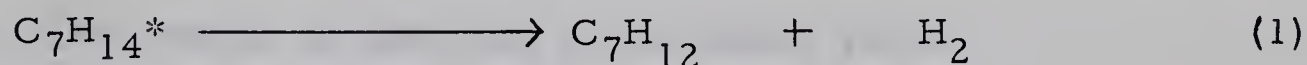
The G-value of MC decreased from 1.95 at zero dose to 1.45





at  $1.8 \times 10^{20}$  ev/g (Figure III-8). Similar behavior was noted in the production of cyclohexene from the radiolysis of cyclohexane vapor (21, 61). The number of possible secondary reactions that could cause this decrease in yield is too large to make speculation worthwhile at this point.

The increase of  $G(\text{MC})$  with decreasing pressure (Figure III-11) cannot be explained by the mechanism



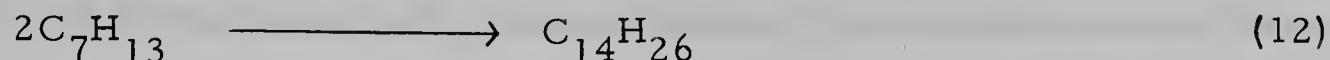
because there is no corresponding increase of  $G(\text{H}_2)$  at low pressure.

The MC yield increased linearly with temperature over the range from  $60^\circ$  to  $260^\circ\text{C}$  (Figure III-14). A similar increase in the cyclohexene yield was found by Blachford and Dyne in their cyclohexane study (61). The increase of  $G(\text{C}_6\text{H}_{10})$  with temperature was attributed to the decreased efficiency of a secondary reaction which destroys cyclohexene. The increase of the MC yield with temperature cannot be due to increased methylcyclohexyl radical production, followed by disproportionation of these radicals to MC and MCH. If this was true then the dimer products from the competing radical combination reaction would also increase at higher temperatures. As shown in Figure III-14 the dimer yields are independent of temperature. In the later discussion of additive effects, further evidence for the destruction of MC by secondary reactions is given.



### b. Total Dimer

The total dimer yield was unaffected by variations of the dose, pressure and temperature in the ranges studied. (See Figures III-8, III-10 and III-14). Bimethylcyclohexyl, the principal dimer, is probably formed by combination of methylcyclohexyl radicals.



Evidence for the formation of dimer by reaction (12) is presented in later discussion of the effects of additives on the dimer yield.

### c. Unknown Products (Unk. $\text{C}_5\text{-C}_6$ )

The yield of these unidentified products decreases with increasing dose as shown in Figure III-8 and shows an increase in yield with decreasing pressure (Figure III-10) and with increasing temperature (Figure III-13). The behavior of the yield with pressure and temperature are similar to the effects observed for olefin products. This observation may give weight to its identification as a  $\text{C}_5$  olefin rather than a  $\text{C}_6$  saturated compound.

## B. Effects of Additives on MCH Radiolysis Products

To account for the dilution effect of the additive the yields of products from the MCH-additive mixtures were calculated on the basis of the energy absorbed by MCH only. This assumes there is no energy transfer from the additive to the solvent. Product yields calculated on this basis are given the symbol g. In MCH- $\text{CCl}_4$  mixtures where there was a number of combination products formed from both the radiolysis of MCH and  $\text{CCl}_4$ , the yields were calculated from the total energy absorbed.



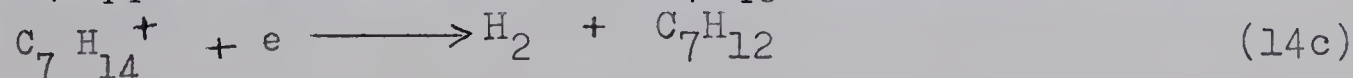
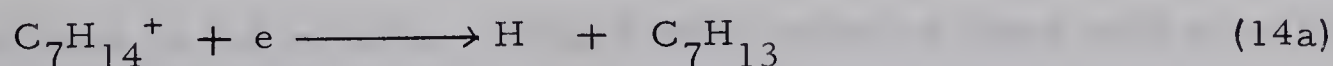
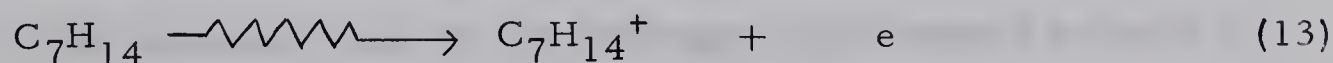


# 1. Hydrogen

## a. Additives - $\text{CCl}_4$ , $\text{N}_2\text{O}$ , $\text{SF}_6$

The three additives,  $\text{CCl}_4$ ,  $\text{N}_2\text{O}$  and  $\text{SF}_6$  all reduced the hydrogen yield from MCH; the reduction in each case was from  $g(\text{H}_2) = 5.3$  in pure MCH to  $g(\text{H}_2) = 3.1 \pm 0.1$  (Figures III-17, III-22 and III-28). In each case, the reduction of  $g(\text{H}_2)$  was complete at a concentration of less than 0.5 mole percent additive. Although there was a large scatter of the experimental points along the plateau region, with  $\text{N}_2\text{O}$  as an additive, there did not appear to be any effect on the reduction of  $g(\text{H}_2)$  by changes in the total pressure of gas in the cell. Similarly, the amount of reduction was the same at  $50^\circ\text{C}$  and  $110^\circ\text{C}$ .

Both  $\text{CCl}_4$  and  $\text{SF}_6$  have large capture cross sections for thermal electrons (100). The reaction of  $\text{N}_2\text{O}$  with thermal electrons to produce nitrogen has been found to occur in a mass spectrometer (101). The identical effect of all three additives on the hydrogen yield suggests these compounds are all interfering with the same precursor of hydrogen. In view of the reactivity of these additives with thermal electrons, the reduction of  $g(\text{H}_2)$  is probably due to scavenging of electrons which in pure MCH result in hydrogen formation. The inhibition of the hydrogen yield can be represented by the following mechanism, where S represents any of  $\text{CCl}_4$ ,  $\text{N}_2\text{O}$  or  $\text{SF}_6$ .









While reaction (14a) has been written involving the  $\text{C}_7\text{H}_{14}^+$  ion, it is probable that at least a portion of the positive ions are in fact fragment ions formed by decomposition of  $\text{C}_7\text{H}_{14}^+$  and other positive ions formed as a result of ion-molecule reactions. To simplify the present discussion, the reactions of positive ions are illustrated using  $\text{C}_7\text{H}_{14}^+$ .

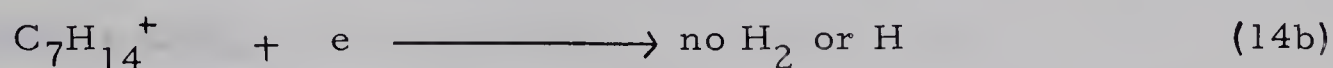
The  $\text{S}^-$  formed in reaction (16) may or may not dissociate upon electron capture. With  $\text{N}_2\text{O}$ , dissociation to  $\text{N}_2$  and  $\text{O}^-$  takes place in a mass spectrometer (101). Dissociative electron capture by  $\text{N}_2\text{O}$  has been postulated in the radiolysis of pure  $\text{N}_2\text{O}$  (115, 30). Nitrogen was observed as a radiolysis product in the MCH- $\text{N}_2\text{O}$  mixtures, however the yield was much larger than can be explained by reaction (16) followed simply by dissociation. The nitrogen yield from MCH- $\text{N}_2\text{O}$  mixtures is discussed in a later section. When S is  $\text{CCl}_4$ , dissociative electron capture occurs and  $\text{CCl}_3$  and  $\text{Cl}^-$  are formed (112). Radiolysis products which could be formed from  $\text{CCl}_3$  are observed in mixtures of MCH plus  $\text{CCl}_4$ . The formation of the chlorinated products is discussed in section IV-C-1.

The total decrease in the hydrogen yield caused by each of these additives is 2.2 g-units. This number must be taken with a certain



degree of caution however, since it is dependent on the yield of hydrogen from pure MCH, and as noted earlier the value of this yield was not completely reproducible. With this reservation, the reduction of  $g(\text{H}_2)$  caused by these electron scavengers may be equated to the yield of electrons which are precursors of hydrogen in pure MCH. The measured W-value of MCH under the conditions of radiolysis was 22.6 ev (Table III-4). This gives a total electron yield of  $G(e) = 4.4$ . Thus only approximately 50 percent of the neutralization processes in pure MCH result in hydrogen formation. In propane radiolysis Johnson and Warman found that approximately 60 percent of the neutralization reactions contribute to the hydrogen yield (76) and in cyclohexane vapor the fraction was estimated to be less than one half (21).

In addition to reaction (14a) the following neutralization reaction must therefore be included in the reaction scheme.



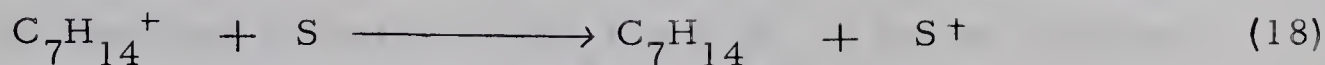
Recall that all the positive ions are represented as  $\text{C}_7\text{H}_{14}^+$  for the present to simplify discussion.

Other methods of reducing  $g(\text{H}_2)$  by these additives seem less likely than electron scavenging. The reaction of hydrogen atoms with  $\text{SF}_6$  (113) and with  $\text{N}_2\text{O}$  (114) is inefficient. The similarity between the effects of  $\text{CCl}_4$  and of  $\text{SF}_6$  and  $\text{N}_2\text{O}$  on the hydrogen yield indicates that  $\text{CCl}_4$  also does not react effectively with hydrogen atoms, at least at compositions less than 10 mole percent  $\text{CCl}_4$ . The charge transfer



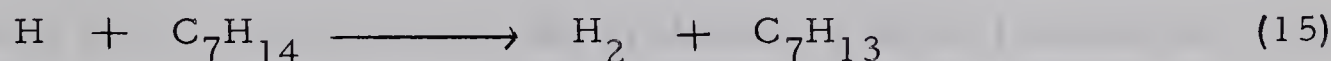
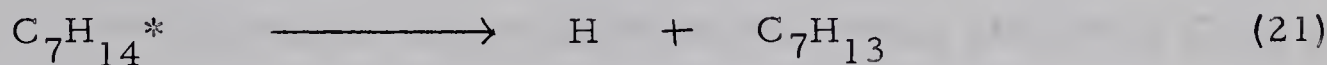
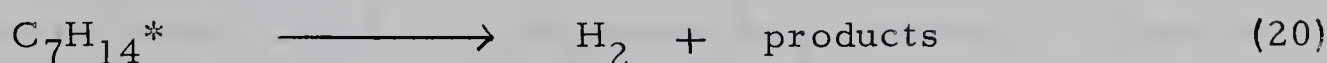


reaction from  $C_7H_{14}^+$  to S



does not occur because the ionization potentials of  $CCl_4$ , 11.5 ev (103),  $N_2O$ , 12.9 ev (103) and  $SF_6$ , 15.8 ev (112) are all greater than that of MCH, 9.85 ev (103) or of its probable fragment ions.

The remaining 3.1 g-units of hydrogen are formed from precursors which do not react with small concentrations of  $CCl_4$ ,  $N_2O$  or  $SF_6$ . Two possible sources of this hydrogen are illustrated by the following reactions



The further decrease of the hydrogen yield at high  $CCl_4$  concentration is discussed in section IV-C-1.

#### b. Additive- $C_2H_4$

In the presence of ethylene, the hydrogen yield from MCH decreased from 5.3 to 1.6 (Figure III-15). The hydrogen yield from the MCH itself is computed from the formula

$$g(H_2)_{MCH} = \frac{G(H_2)_{Total} - G(H_2)_{C_2H_4} \epsilon_{C_2H_4}}{\epsilon_{MCH}}$$

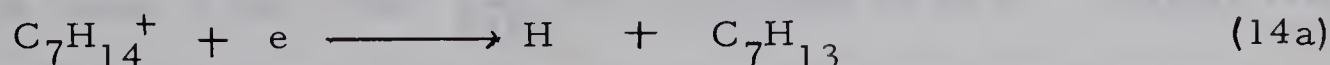
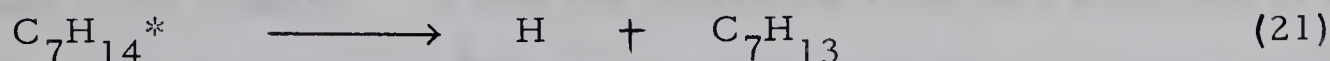
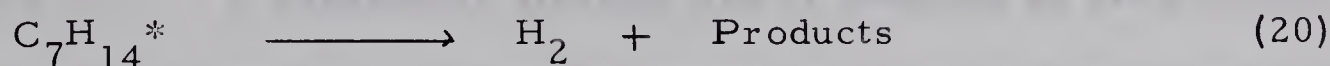
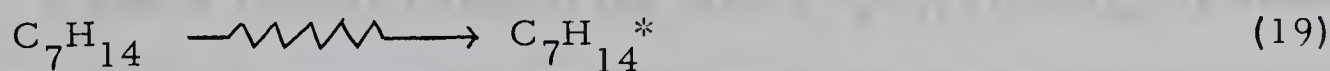
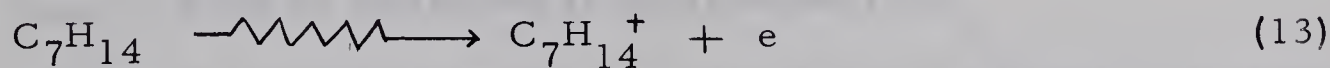
where  $\epsilon$  = electron fraction of either  $C_2H_4$  or MCH; and  $G(H_2)_{C_2H_4} = 1.3$  is the yield of hydrogen from pure ethylene and is assumed to be unaffected by the presence of MCH.



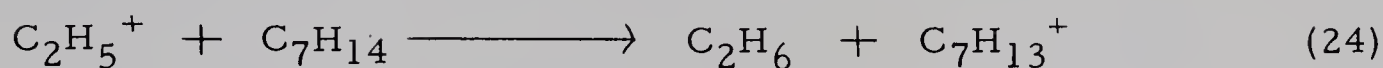
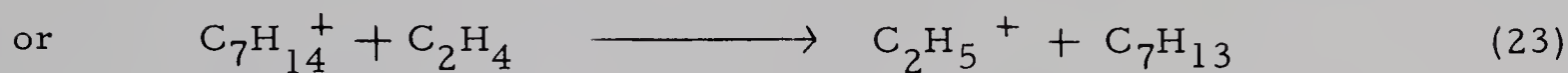
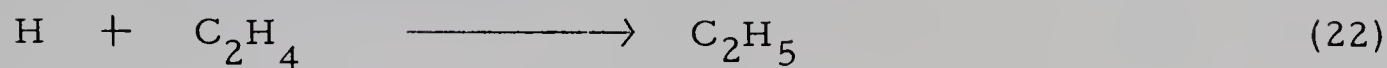
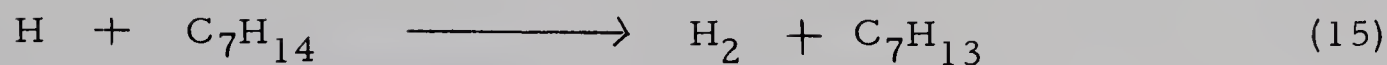
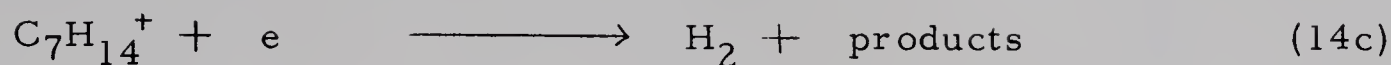
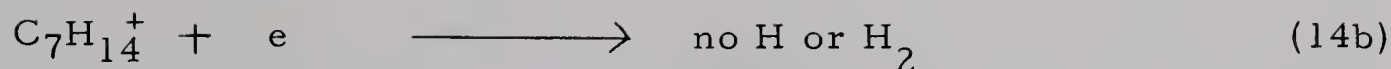


Since ethylene has little tendency to capture electrons, it is unlikely the observed decrease of  $g(H_2)$  by  $C_2H_4$  is due to electron scavenging. Charge transfer is ruled out because the ionization potential of  $C_2H_4$  is higher than that of MCH, 10.5 eV compared to 9.85 eV. The proton affinity of  $C_2H_4$  is quite large, 153 kcal/mole (calculated from thermochemical data (110)) and proton transfer reactions to olefins from positive ions have been suggested (104). The feasibility of a proton transfer mechanism depends upon the proton affinity of  $C_7H_{13}$ . If the proton affinity of  $C_7H_{13}$  is less than the proton affinity for  $C_2H_4$  the proton transfer from  $C_7H_{14}^+$  to  $C_2H_4$  would be exothermic. There is insufficient thermochemical data to estimate the proton affinity of  $C_7H_{13}$  but the value of 151 kcal/mole for the cyclohexyl radical (calculated from thermochemical data (110, 116)) indicates that the proton transfer reaction would be close to thermoneutral. Ethylene also reacts readily with hydrogen atoms (105) so can function as a hydrogen atom scavenger in MCH radiolysis.

Two equivalent mechanisms can be written to explain the reduction of the hydrogen yield by ethylene







In both these mechanisms the portion of the hydrogen yield that cannot be scavenged by  $\text{C}_2\text{H}_4$  is suggested to arise from reaction (20).

From a steady state kinetic treatment of the hydrogen atom scavenging reaction, the following equation can be obtained

$$\frac{1}{\Delta g(\text{H}_2)} = \frac{1}{g(\text{H}_2) - g(\text{H}_2)'} = \frac{1}{g_{\text{H}} + \frac{k_{14a} + k_{14c}}{k_{14a} + k_{14b} + k_{14c}} g_{\text{ion}}} \left[ 1 + \frac{k_{22}}{k_{15}} \frac{[\text{C}_2\text{H}_4]}{[\text{C}_7\text{H}_{14}]} \right]$$

where,  $g(\text{H}_2)$  = measured hydrogen yield from MCH- $\text{C}_2\text{H}_4$  mixtures,

$g(\text{H}_2)' = 1.6$  = yield of hydrogen nonscaveneable by ethylene,

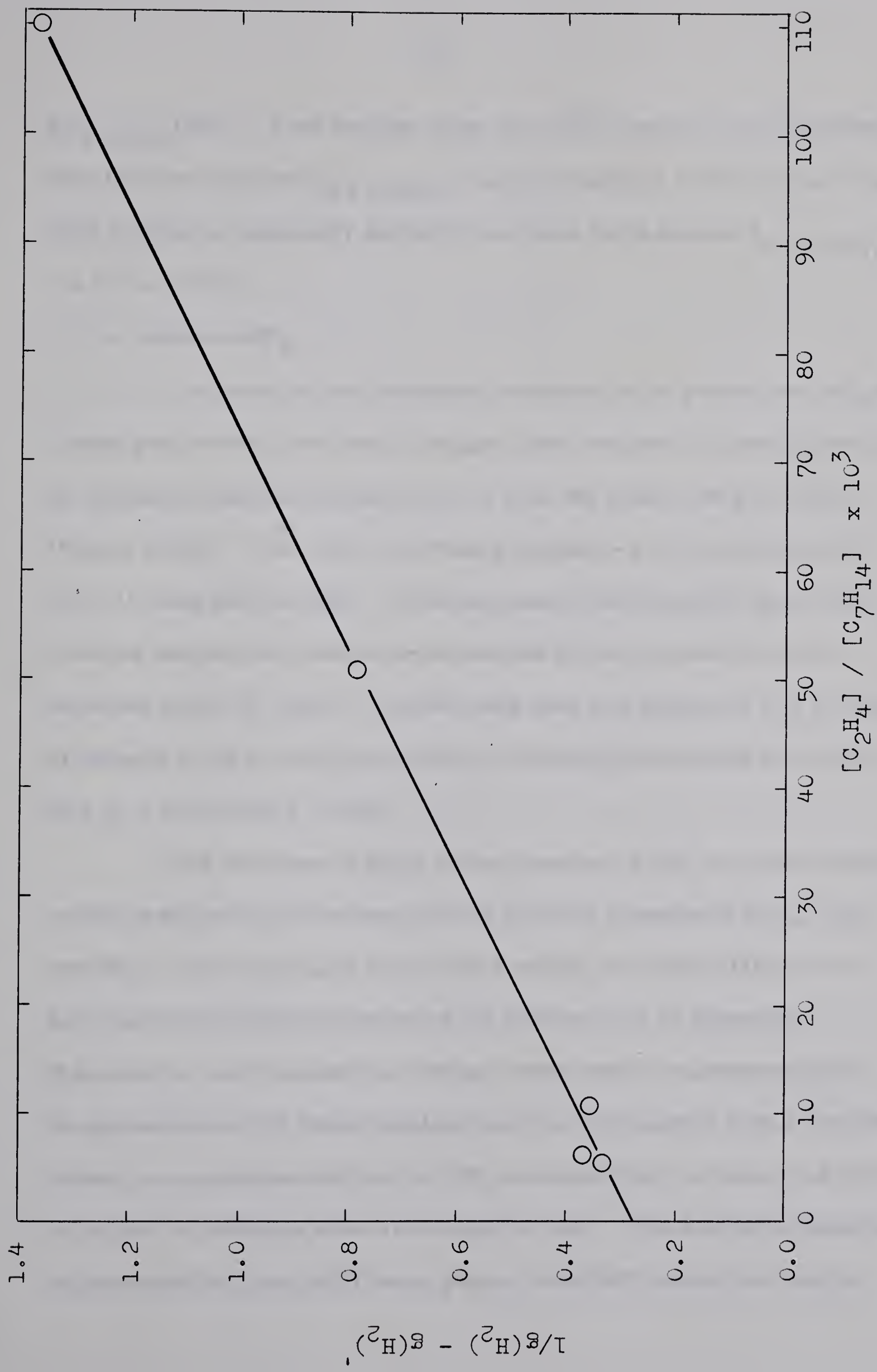
$g_{\text{H}}$  = yield of hydrogen atoms from reaction (21),

$g_{\text{ion}}$  = yield of ionization from reaction (13).

A plot of  $1/\Delta g(\text{H}_2)$  against the ratio  $[\text{C}_2\text{H}_4]/[\text{C}_7\text{H}_{14}]$  is shown in Figure IV-1. A reasonably straight line is obtained as predicted by the steady state equation. From the measured slope and intercept of the line, the value of ratio rate  $\frac{k_{22}}{k_{15}}$  was calculated to be 37. Values from  $10^7$  to  $10^9$  l-mole $^{-1}$ sec $^{-1}$  have been reported for the rate constant

FIGURE IV - 1

Kinetic Plot for Hydrogen Yield in MCH-C<sub>2</sub>H<sub>4</sub> Mixtures







$k_{H + C_2H_4}$  (105). If an average value of  $\sim 10^8$  l-mole<sup>-1</sup> sec<sup>-1</sup> is assumed, then the rate constant  $k_{H + C_7H_{14}}$  is approximately  $3 \times 10^6$  l-mole<sup>-1</sup> sec<sup>-1</sup>. This compares reasonably well with the value for isobutane  $k_{H + iC_4H_{10}} \approx 9 \times 10^6$  at 110°C.

### c. Additive-ND<sub>3</sub>

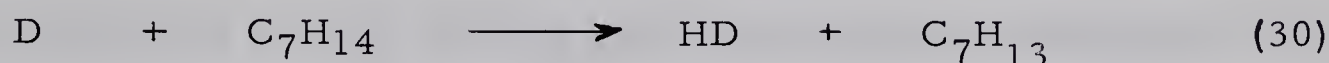
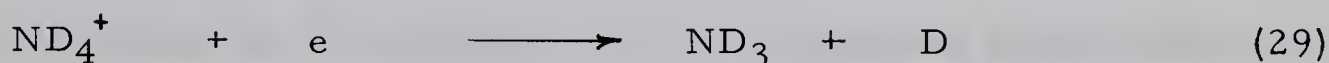
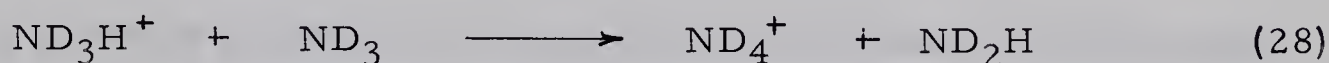
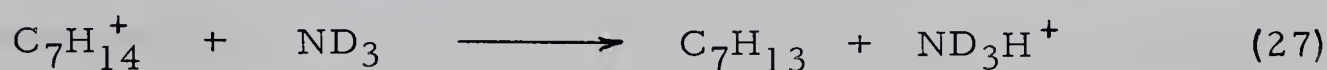
The yield of total hydrogen increased in the presence of ND<sub>3</sub> at 1 mole percent ND<sub>3</sub>, the total hydrogen yield reached a plateau of  $g=6.6$ , an increase of  $g(\text{total hydrogen})$  of 1.3 over the yield from pure MCH (Figure III-30). The value of  $g(\text{total hydrogen}) = 6.6$  was maintained up to 10 mole percent ND<sub>3</sub>. This increase in the total hydrogen yield resulted because the yield of newly formed HD was greater than the decrease of the H<sub>2</sub> yield. The HD yield rose to a plateau of 3.4 g-units at between 1 and 2 mole percent ND<sub>3</sub>, while  $g(H_2)$  decreased to a value of 3.2, i.e. by only 2.1 units.

The decrease of  $g(H_2)$  in the presence of ND<sub>3</sub> was very similar to that observed in the presence of the electron scavengers CCl<sub>4</sub>, N<sub>2</sub>O and SF<sub>6</sub>. The scavenging of electrons by ND<sub>3</sub> is unlikely (106), therefore interference with reactions of the positive ions is suggested. Because the rate constant for hydrogen atom attack on ammonia (107) is approximately 100 times smaller than that for reaction with a saturated alkane, in conjunction with the low ND<sub>3</sub> concentration, the observed effect is not due to hydrogen atom scavenging by ND<sub>3</sub>. The ionization potential of ammonia (10.2 eV) (103) being greater than MCH makes the charge



transfer reaction from  $C_7H_{14}^+$  to  $ND_3$  endothermic. The large proton affinity of ammonia,  $174 \text{ kcal-mole}^{-1}$  (104), indicates that proton transfer from  $C_7H_{14}^+$  to  $ND_3$  is the probable scavenging reaction.

Proton transfer to  $ND_3$  was proposed by Williams (106) to explain the formation of HD in the radiolysis of liquid cyclohexane with added  $ND_3$ . A similar proton transfer mechanism consisting of reactions (13, 14 and 15) followed by reactions (27, 28, 29 and 30) below is proposed to account for the decrease of  $g(H_2)$  and the formation of HD.



The exchange reaction (28) between  $ND_3H^+$  and  $ND_3$  has been shown to be fast;  $k_{28} \approx 10^{12} \text{ l-mole}^{-1} \text{ sec}^{-1}$  (66), in the mass spectrometer.

This mechanism suggests that if all the positive ions produced react by proton transfer to  $ND_3$  the yield of HD should be equal to the yield of positive ions, i.e.  $G = 4.4$ . The plateau value of  $g(HD) = 3.4$  indicates that all the positive ions are not scavenged by  $ND_3$ . The presence of ions which do not donate a proton could account for the lower yield of HD compared to the total ionization yield. An alternative explanation is that the exchange reaction (28) does not occur at all in this system and the positive ammonium ion in the neutralization reaction (29) is  $ND_3H^+$  rather than  $ND_4^+$ . Assuming no isotope effect, then the yield of HD





should be  $4.4 \times 3/4 = 3.3$ , which is close to the observed HD yield. If the exchange reaction does not occur the yield of  $H_2$  from the neutralization of  $ND_3H^+$  should be  $g \approx 1.1$ . From the electron scavenger studies with  $CCl_4$ ,  $N_2O$  and  $SF_6$  the non ionic yield of  $H_2$  was 3.1. Since  $ND_3$  cannot interfere with this non-ionic yield of  $H_2$ , then the total  $g(H_2)$  in the presence of  $ND_3$  should be  $3.1 + 1.1 = 4.2$ . The observed  $g(H_2) = 3.2$  is close to non ionic yield of  $H_2$  yield which indicates that the exchange reaction (29) does take place and the low HD yield is due to positive ions that cannot donate a proton to  $ND_3$ .

The value of  $g(HD) = 3.4$  exceeds the decrease of the  $H_2$  yield ( $\Delta g(H_2) = 2.1$ ) caused by  $ND_3$  addition. If, as suggested by the similarity between the reduction of  $g(H_2)$  by  $ND_3$  and by the electron scavengers  $CCl_4$ ,  $N_2O$  and  $SF_6$ , the yield of  $H_2$  from ionic precursors in pure MCH is  $2.2 \pm 0.1$  g-units, then  $ND_3$  scavenges 1.2 g-units of positive ions that are not precursors of hydrogen in pure MCH radiolysis.

#### d. Additive-DI

The addition of 2-3 mole percent of DI increased the total hydrogen yield by 1.1 g-units over the yield from pure MCH (Figure III-32). This increase in total hydrogen yield was similar to the increase observed when  $ND_3$  was used as an additive. The  $H_2$  yield decreased from  $g = 5.3$  in pure MCH to a plateau value of  $g = 1.6$  at 1-2 mole percent DI. The magnitude of the decrease was the same as that caused by  $C_2H_4$  addition, but with DI the reduction was complete at a concentration 30 times lower





than with  $C_2H_4$ . The decrease of  $g(H_2)$  is more than balanced by the formation of HD and  $D_2$ , resulting in the overall increase of the total hydrogen yield.

Hydrogen iodide is an efficient hydrogen atom scavenger (105). If DI acts solely as a hydrogen atom scavenger, as was suggested for  $C_2H_4$ , then the HD yield should be equal to the decrease of  $g(H_2)$ . Because  $g(HD) = 2.5$  is much less than  $\Delta g(H_2) = 3.7$ , and because a large amount of  $D_2$  is formed, DI does not act solely as a hydrogen atom scavenger.

Charge transfer from  $C_7H_{14}^+$  to DI is unlikely since the reaction is endothermic. The ionization potential of DI is 10.4 eV compared with 9.85 eV for MCH (103). The proton affinity of HI is 117 kcal/mole (104). Since this is much lower than the probable proton affinity of  $C_7H_{13}$  (see part b), proton transfer from  $C_7H_{14}^+$  to DI is unlikely.

Electron capture by HI is known to occur (108). Thus DI probably affects the production of hydrogen by a combination of hydrogen atom and electron scavenging.

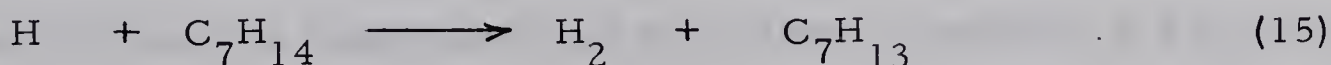
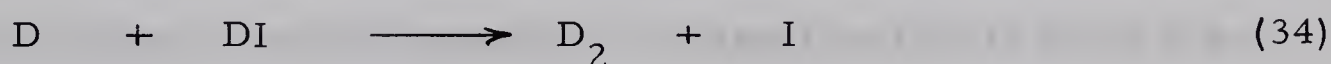
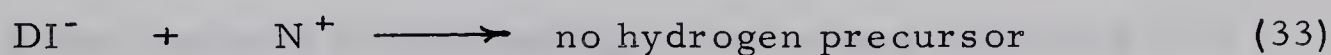
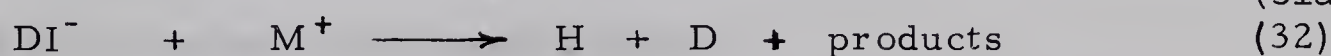
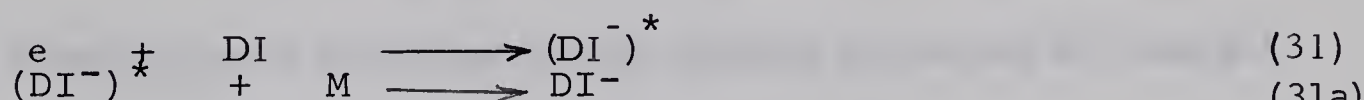
To postulate a mechanism for the formation of  $H_2$ , HD and  $D_2$  in MCH-DI mixtures, it is necessary to estimate the relative contributions of various hydrogen precursors to the total hydrogen yield,  $g = 6.4$ , observed at high DI concentration. From the amount of  $H_2$  that cannot be scavenged by DI or by  $C_2H_4$  the value of  $g$  (unscavengeable  $H_2$ ) is 1.6. This unscavengeable or molecular hydrogen is formed by reaction (20). The contribution of H atoms from reaction (21) can be estimated from the



results with the electron scavengers  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ ,  $\text{CCl}_4$ , and the molecular hydrogen yield. In the systems, MCH-electron scavenger the unscavengable  $g(\text{H}_2)$  is 3.1; of this, 1.6 is due to molecular hydrogen, therefore the remainder  $g = 1.5$  is due to H atoms. This leaves 3.3 g-units of the total hydrogen that arise from the ionization process reaction (13).

In pure MCH radiolysis it was estimated that only 50 percent of the total ions produced resulted in hydrogen formation. In the presence of DI the fraction of total yield of ions (4.4) that are hydrogen precursors is 0.75. Thus with added DI, as with added  $\text{ND}_3$ , a greater fraction of the ions yield hydrogen than they do in the pure MCH system.

The following mechanism is suggested to account for the formation of  $\text{H}_2$ , HD and  $\text{D}_2$  in MCH-DI mixtures. Reactions (13), (14), (19), (20), (21) followed by



where  $\text{M}^+$  and  $\text{N}^+$  are unspecified hydrocarbon ions.

At high DI concentration where the yield of total hydrogen reaches a plateau, all of the electrons are scavenged by DI to form  $\text{DI}^-$ .





The bond energy for DI is approximately 72.8 kcal/mole, estimated from BDE (H—I) = 71.3 kcal/mole (116) plus  $\sim 1.5$  kcal/mole for the zero-point energy difference between HI and DI. This value of 72.8 kcal/mole for BDE (DI) compared with the electron affinity of I, 72.3 kcal/mole (117), indicates that  $\text{DI}^-$  may not dissociate. If dissociative electron capture did occur then the yield of total hydrogen due to electrons should be 4.4 g-units, which is inconsistent with the observed results. The proposed mechanism suggests that a fraction of the scavenged electrons are lost as hydrogen precursors in the neutralization of  $\text{DI}^-$  with unspecified ions designated as  $\text{N}^+$ . The ions of type  $\text{N}^+$  also correspond to the ions which did not donate a proton to  $\text{ND}_3$  in the MCH- $\text{ND}_3$  system. The yield of  $\text{N}^+$  type ions estimated from the MCH-DI mixtures is 1.1 g-units compared to 1.0 units estimated from the MCH- $\text{ND}_3$  mixtures. There is not sufficient information to speculate on the identity of the ion  $\text{M}^+$  and  $\text{N}^+$  except that  $\text{N}^+$  is probably hydrogen deficient.

From the yield of total hydrogen that arises from ions (3.3 g-units), the fraction of the  $\text{DI}^-$  that react via reaction (32) to form H and D atoms is  $3.3/4.4 = 0.75$ . If it is assumed that at high DI concentration the plateau yield of  $\text{D}_2$  observed is due to the D atoms reacting exclusively by reaction (34) then the maximum yield of D atoms is equal to 2.3 g-units. Therefore the fraction of D atoms produced in reaction (32) is  $2.3/3.3 = 0.70$ . The hydrogen precursors H and D then react with either  $\text{C}_7\text{H}_{14}$  or DI to form  $\text{H}_2$ , HD and  $\text{D}_2$  according to reactions (15), (34), (35) and (36).





The increase in the total hydrogen yield observed when DI is added to MCH arises from ionic precursors that do not give hydrogen in pure MCH. By using the variation of the total hydrogen yield with DI concentration (Figure III-32 A) as a measure of the fraction of electrons scavenged and assuming values for  $k_{34}/k_{35}$  and  $k_{36}/k_{15}$ , the yield of  $H_2$ , HD and  $D_2$  at different DI concentrations can be calculated. The following values of the relative rate constants were found to give the best fit with the experimental results.

$$k_{34}/k_{35} = \frac{k_{D+DI}}{k_{D+C_7H_{14}}} = 1.2 \times 10^3$$

$$k_{36}/k_{15} = \frac{k_{H+DI}}{k_{H+C_7H_{14}}} = 8.6 \times 10^2$$

These values are of the same order of magnitude as the value of  $k_{D+HI}/k_{D+C_6D_{12}} \approx 5 \times 10^3$  found in the liquid phase radiolysis of HI- $C_6D_{12}$  solutions by Nash and Hamill (109).

The calculated yield composition curves  $H_2$ , HD and  $D_2$  are shown as the solid lines in Figure III-32. The experimentally determined values are shown as points in the same Figure. The agreement of the calculated yields with the measured yields is quite good.

Further information relating to the formation of HD and  $D_2$  in MCH-DI mixtures is presented in the following section of competition studies between DI and other scavengers in MCH.



## e. Additive Competition Studies

i. MCH-DI- $C_2H_4$ 

If the  $D_2$  in MCH-DI mixtures was formed with a D atom as the immediate hydrogen precursor, and if the HD was formed as suggested in the previous section, then the addition of  $C_2H_4$  to MCH-DI should reduce the yield of both HD and  $D_2$ . The  $H_2$  yield if formed by reaction (20) should be unaffected by the presence of  $C_2H_4$ . Figure III-34 illustrates that this behaviour is observed. The slow decrease of HD and  $D_2$  yields with increasing  $C_2H_4$  concentration indicates that the reaction of hydrogen atoms with  $C_2H_4$  is less efficient than the reaction of hydrogen atoms with DI. This is consistent with the rate constants,  $k_{H+DI} \approx 10^9 \text{ l-mole}^{-1} \text{ sec}^{-1}$  and  $k_{H+C_2H_4} \approx 10^8 \text{ l-mole}^{-1} \text{ sec}^{-1}$  by Thrush (105).

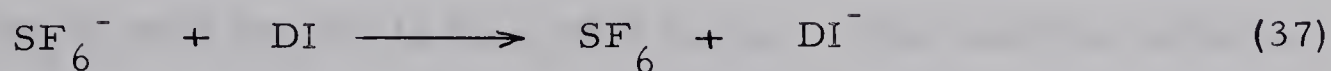
ii. MCH-DI- $SF_6$ 

The  $D_2$  yield in MCH-DI mixtures was suggested to be the result of electron capture by DI. The presence of a second electron scavenger such as  $SF_6$  in the MCH-DI system should compete with DI for the electrons, causing a reduction in the  $D_2$  yield. If, as suggested, a portion of HD yield from the radiolysis of MCH with added DI was formed as a result of electron scavenging by DI then a portion of the HD yield should also be removed by  $SF_6$ . The  $H_2$  yield should be unaffected by  $SF_6$ . Qualitatively Figure III-35 shows this does occur. The  $D_2$  yield from the 1% DI solution is reduced to zero, the HD yield is partially reduced and  $g(H_2)$  is unaffected. Quantitatively, however, there are some disturbing aspects





shown in Figure III-35. The reduction of  $g(D_2)$  to zero requires a 10 fold excess of  $SF_6$  over DI. In MCH- $SF_6$  mixtures the scavenging of electrons by  $SF_6$  was complete at approximately 0.1 mole percent  $SF_6$  (Figure III-28); in MCH-DI mixtures, electron scavenging was not complete until 3-4 mole percent DI had been added (Figure III-32). If, as suggested, both DI and  $SF_6$  were reacting with electrons, then a comparison of Figures III-28 and III-32 suggests that  $SF_6$  is 30-40 times more effective than DI. This is approximately a factor of 10 greater than the relative rates for electron capture observed when  $SF_6$  and DI are present in the system together. The reason for this effect is not obvious. HI has been shown to capture electrons with a wider energy range than does  $SF_6$  (111). HI captures electrons of energy from 0.03 to 0.53 ev, with the maximum capture efficiency at 0.05 ev. The range of electron energy for capture by  $SF_6$  is zero to about 0.03 ev, with a maximum capture cross section for electrons of zero ev. It is possible that DI may capture electrons at the higher energies, before the energy has been decreased to the range required for capture by  $SF_6$ . This could account for the inefficiency of  $SF_6$  as an electron scavenger in the presence of DI. An alternative explanation may be electron capture initially by  $SF_6$  followed by electron transfer to DI before neutralization.



This reaction would require the electron affinity of DI to be greater than that of  $SF_6$ .



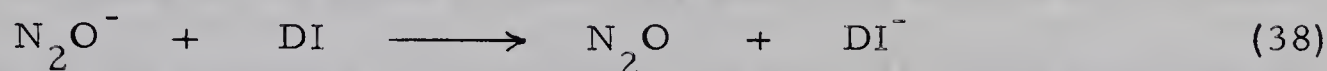


iii. MCH-DI-N<sub>2</sub>O

As shown in Figure III-36 the addition of N<sub>2</sub>O to MCH-DI mixtures does not change any of the hydrogen yields. Furthermore, nitrogen was not formed, which indicates that N<sub>2</sub>O could not compete with DI for electrons. In fact, as illustrated by the first appearance of N<sub>2</sub> at a ratio of  $[N_2O / DI] = 1.5 \times 10^3$  (Figure III-37), competition does not occur until there is a very large excess of N<sub>2</sub>O. This is in contrast to the relative electron scavenging ability of N<sub>2</sub>O and DI shown by a comparison of Figures III-22 and III-32. Electron scavenging by N<sub>2</sub>O in MCH-N<sub>2</sub>O mixtures was complete at 0.3 mole per cent N<sub>2</sub>O while in MCH-DI mixtures all the electrons were not scavenged by DI until 3 mole per cent DI. Thus, similar to the observations with SF<sub>6</sub>, the efficiency of N<sub>2</sub>O as an electron scavenger is much smaller in the presence of DI than when it is alone in MCH. The capture of electrons of higher energy as suggested in the case of SF<sub>6</sub> cannot explain the behavior of N<sub>2</sub>O. N<sub>2</sub>O has its greatest efficiency for electron capture at 0.7 ev (111), which is above the maximum electron energy for capture by DI. If the lifetime of N<sub>2</sub>O<sup>-</sup> before dissociation to N<sub>2</sub> + O<sup>-</sup> is long enough, then DI may interfere with N<sub>2</sub>O<sup>-</sup> and prevent the formation of nitrogen. Curran and Fox (101) have measured the bond dissociation energy of N<sub>2</sub>O, BDE (N<sub>2</sub>-O) to be  $1.34 \pm 0.2$  ev. The electron affinity of an O atom is 1.47 ev (117). Taking BDE (N<sub>2</sub>-O) = 1.34 dissociative electron capture by N<sub>2</sub>O is exothermic, but if the upper limit of the bond



dissociation energy, 1.54 eV, is taken, then dissociative electron capture is endothermic. Thus there is a possibility that  $\text{N}_2\text{O}^-$  could live long enough to undergo reaction with DI. The reaction cannot be simply electron transfer from  $\text{N}_2\text{O}^-$  to DI



since this should result in a total hydrogen increase to  $g = 6.4$ . (The value found in the MCH-DI system for complete electron scavenging.) However, the increase of  $g(\text{H}_2)$  and  $g(\text{HD})$  by DI plus the small yield of  $\text{N}_2$  remaining at 0.012 mole percent DI in the MCH- $\text{N}_2\text{O}$  mixture can only account for a fraction of the total electrons. Thus DI is interfering with the formation of nitrogen from  $\text{N}_2\text{O}^-$  but in doing so does not yield hydrogen or a precursor of hydrogen in return.

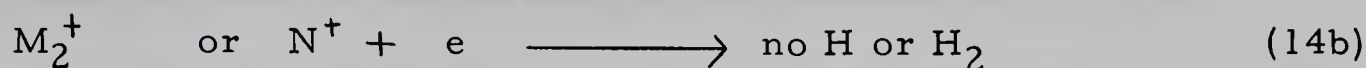
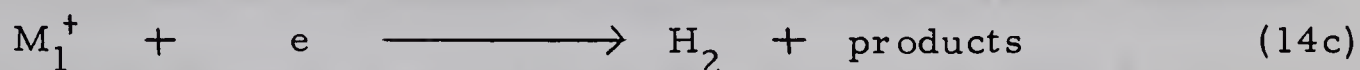
#### f. Summary

On the basis of the above discussion, the hydrogen yield from the radiolysis of MCH vapor arises from three different sources, ions, hydrogen atoms, and molecular hydrogen. The molecular hydrogen has a yield of  $g = 1.6$ , and is probably formed in the unimolecular decomposition of an excited MCH molecule or in the fragmentation of the  $\text{C}_7\text{H}_{14}^+$  ion. Approximately 1.5 g-units of hydrogen are formed from hydrogen atoms that do not have ionic precursors. The remainder of the hydrogen yield,  $g = 2.2$ , arises from the neutralization reaction of ions. In the presence of scavengers  $\text{ND}_3$  and DI and additional yield of hydrogen,  $g = 1.2$ , is obtained from ionic precursors. From the total yield of ions  $g = 4.4$ ,



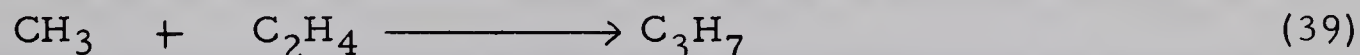


approximately 1.0 g-units do not form hydrogen even in the presence of  $\text{ND}_3$  or DI. From the interpretation suggested to account for hydrogen formation in MCH, there must be three different types of positive ions in the system. Ion  $\text{N}^+$  does not yield hydrogen under any circumstances; ion  $\text{M}^+$  consists of two types of ions,  $\text{M}_1^+$  and  $\text{M}_2^+$ , both of which yield hydrogen in the presence of DI or  $\text{ND}_3$ , but only  $\text{M}_1^+$  yields hydrogen in pure MCH. Therefore, reactions (14a) and (14b) should be written as



## 2. Methane

The yield of  $\text{CH}_4$  from MCH was unaffected by the addition of the ion scavengers  $\text{N}_2\text{O}$ ,  $\text{SF}_6$  and  $\text{ND}_3$ . With added ethylene the observed decrease of  $g(\text{CH}_4)$  (Figure III-15) is probably due to scavenging of methyl radicals by  $\text{C}_2\text{H}_4$ .



The reduction of  $g(\text{CH}_4)$  by DI and the formation of  $\text{CH}_3\text{D}$  (Figure III-33) is also consistent with the scavenging of methyl radicals.

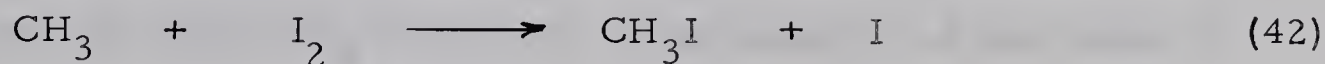
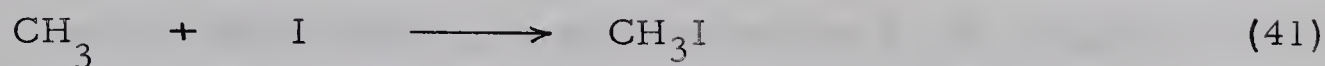


The slow increase of  $g(\text{CH}_3\text{D})$  with increasing DI concentration compared to the rapid decrease of  $g(\text{CH}_4)$ , and the smaller plateau yield of  $\text{CH}_3\text{D}$  compared to the total decrease of the  $g(\text{CH}_4)$  yield indicates there is another scavenging reaction for methyl radicals. Since I atoms and  $\text{I}_2$  are present in the system from the decomposition of DI (51, 120).





additional scavenging reactions could be



In the analysis of the radiolysis products from the MCH-DI systems,  $\text{CH}_3\text{I}$  would be included with the unknown  $\text{C}_5\text{-C}_6$  products, since they both have the same retention time on the gas chromatographic column. The measured increase in the  $\text{C}_5\text{-C}_6$  yield at less than 1 percent DI (Figure III-33), if due to the formation  $\text{CH}_3\text{I}$  would not be a true indication of the  $\text{CH}_3\text{I}$  yield because the sensitivity of the detector for  $\text{CH}_3\text{I}$  is approximately one half that of cyclohexane, which was used for estimating the  $\text{C}_5\text{-C}_6$  yield.

The fact that DI does not reduce the  $\text{CH}_4$  yield to zero indicates a second source of methane formation. This additional  $\text{CH}_4$  yield could arise from the unimolecular decomposition of an excited molecule or ion. The formation of molecular methane in the radiolysis of propane- $\text{d}_8$  from the unimolecular decomposition of  $\text{C}_3\text{D}_8^+$  has been suggested by Ausloos and Lias (56).

The small decrease of  $g(\text{CH}_4)$  up to 5 mole percent  $\text{CCl}_4$  may result from interference with the process forming methyl radicals. Since  $\text{CCl}_4$  was suggested to act as an electron scavenger, the change in the neutralization process may reduce the amount of fragmentation of the MCH molecule to methyl radicals. Above 5 mole percent,  $\text{CCl}_4$  appears to be acting only as a diluting solvent.

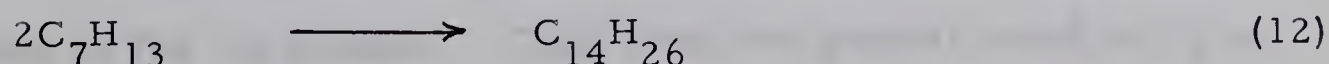
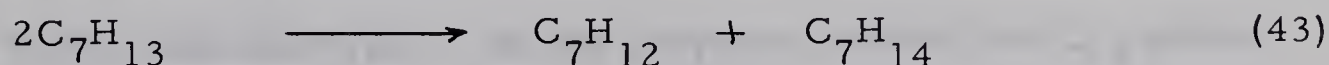


### 3. C<sub>2</sub>-C<sub>3</sub> Products

The only MCH additive system where the C<sub>2</sub>-C<sub>3</sub> products were analysed was in MCH-CCl<sub>4</sub> mixtures. The behavior of the yields of these different gases with increasing CCl<sub>4</sub> concentration was similar. The yields were rapidly decreased at concentrations of CCl<sub>4</sub> less than 10 percent, above which the decrease was essentially a dilution effect. Since all of these products must be formed from the break up of the ring structure of MCH, the similar effect of CCl<sub>4</sub> on the yield of each product suggests that CCl<sub>4</sub> reduced the extent of ring fragmentation. The addition of CCl<sub>4</sub> to MCH changes the neutralization process from positive ion-electron to positive ion-chloride ion. The change in the negative species could result in a smaller amount of fragmentation of the MCH following neutralization.

### 4. Methylcyclohexene (MC) and Total Dimer

When DI is added to MCH the yields of both MC and dimer decrease with increasing DI concentration (Figure III-33), in contrast to the total hydrogen yield which increased with added DI. Since DI can scavenge radicals (121) and the electron precursors of radicals (reaction (14a)), the decrease of both MC and dimer with added DI is consistent with their formation at least in part from the reactions



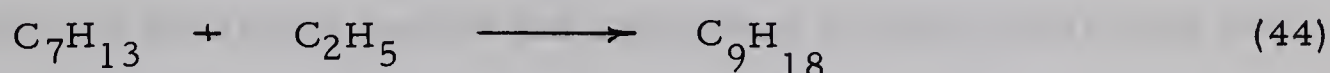
The reduction of g(dimer) to zero by DI suggests that dimer is formed





entirely by reaction (12). The 0.7 g-units of MC that is unscavengable by DI indicates an additional source of MC. One possibility for this additional source is reaction (20). The yield of  $H_2$  from reaction (20) is  $g = 1.6$ ; the observation that the yield of molecular MC is only  $g = 0.7$  indicates that either a part of the molecular MC yield was destroyed by secondary reactions, or that  $C_7H_{14}^*$  in reaction (20) can decompose to  $H_2$  plus products other than MC.

Ethylene or  $ND_3$  addition to MCH increased the MC yield (Figure III-16 and III-31). The dimer yield was also increased by  $ND_3$  but was reduced to zero by ethylene. Above 5 mole percent ethylene the enhanced MC yield decreased with increasing ethylene concentration. This fall off  $g(MC)$  from the maximum, the inhibition of dimer formation and the observed formation of a  $C_9$  product are all consistent with scavenging of  $C_7H_{13}$  radicals by ethyl radicals formed in reaction (22).



The contribution of reaction (46) to the disproportionation reaction is expected to be small. The ratio of disproportionation to combination for  $C_7H_{13}$  radical is approximately 3-4 (87) compared with  $\approx 0.2$  for  $C_2H_5$  radicals (122). In the ethylene system the  $C_{14}$  dimer is replaced by the  $C_9$  product. Thus from the greater yield of  $C_9$  in MCH- $C_2H_4$  mixtures compared to  $C_{14}$  in pure MCH there is also an

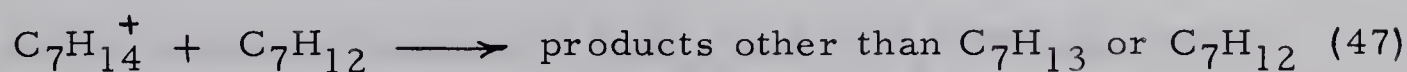




increase in "dimer" as was found by  $\text{ND}_3$  addition.

The increase of MC and dimer by ethylene and  $\text{ND}_3$  indicates that these additives interfere with some secondary reaction that destroys these products and/or their radical precursors. Although ethylene can scavenge H atoms, the involvement of H atoms in the secondary reaction or reactions can be ruled out by the effect of other additives on the MC yield. The addition of  $\text{ND}_3$  prevents the formation of an H atom but substitutes a D atom (reactions 14a, 27, 28, 29) so if the secondary reactions did involve an H atom,  $\text{ND}_3$  should not interfere. In fact, the  $\text{ND}_3$  should have actually favored the destruction of MC by H (or D) atom attack because there is an additional supply of D atoms produced by  $\text{ND}_3$  scavenging positive ions that are not precursors of H atoms in pure MCH. The fact that  $\text{SF}_6$ , which scavenges the electron precursors of H atoms, had no effect on the MC or dimer yields is further evidence that H atoms are not taking part in the secondary reactions affecting MC and dimer yields. Since  $\text{ND}_3$  and  $\text{C}_2\text{H}_4$  can both react with positive ions it is probable that the destruction of MC and dimer and/or the  $\text{C}_7\text{H}_{13}$  radicals is due to positive ions.

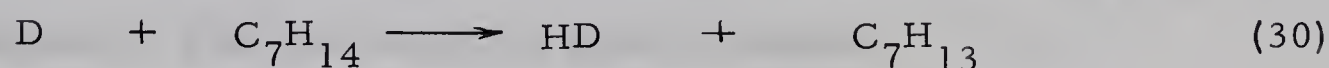
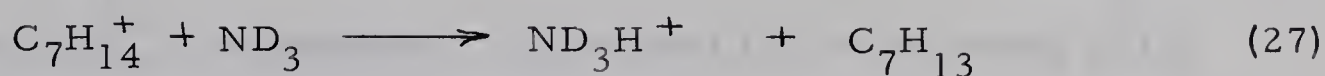
Assume the following secondary reaction,



to be in competition with the neutralization of the positive ion to yield a  $\text{C}_7\text{H}_{13}$  radical reaction (14a). In addition to destruction of MC already formed, reaction (47) reduces both MC and dimer by reducing the number

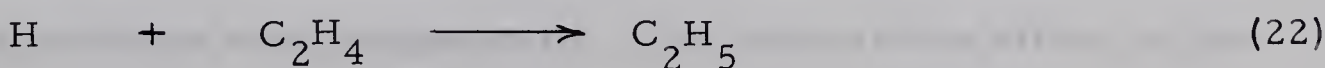
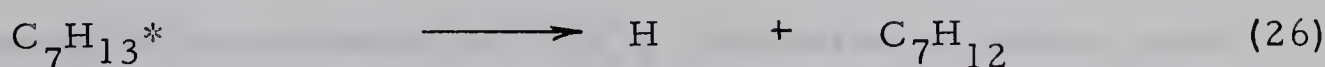
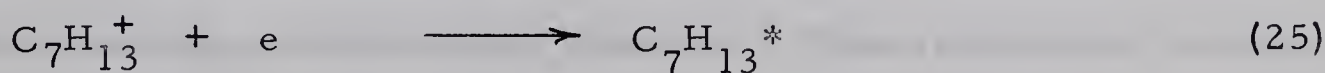
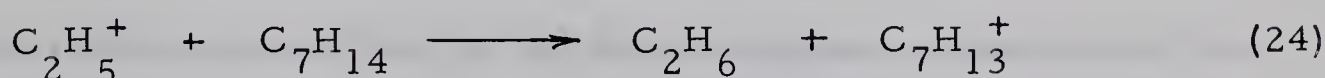
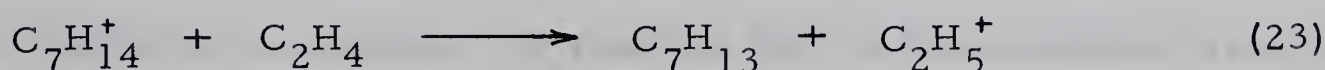


of  $C_7H_{13}$  radicals. In the presence of  $ND_3$ , the following reactions occur.



The effect of  $ND_3$  is to prevent the destruction of MC and  $C_7H_{14}^+$  in reaction (47) and so increase the number of radicals. Therefore the MC and dimer yields in the presence of  $ND_3$  should go up. The fact that  $ND_3$  scavenges a greater number of positive ions than are precursors to radicals in pure MCH was shown in the discussion of the hydrogen yield.

There are a number of possible reactions between positive ions and olefins such as ethylene (69, 73, 104). The proton transfer mechanism considered in the hydrogen discussion could inhibit reaction (47).



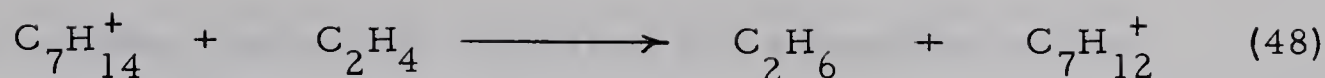
The effect of ethylene acting by this mechanism results in an increased MC yield and an increased number of  $C_7H_{13}$  and  $C_2H_5$  radicals, which would account for the increased yield of "dimer" product.

An alternative reaction of the positive ion with ethylene is the  $H_2$  transfer reaction (73).









The fate of  $\text{C}_7\text{H}_{12}^+$  is unknown. To account for the increase of  $\text{C}_9$  "dimer" yield, as well as the increase in MC yield in MCH- $\text{C}_2\text{H}_4$  mixtures subsequent reactions of  $\text{C}_7\text{H}_{12}^+$  must result in an increase of  $\text{C}_2\text{H}_5$  or  $\text{C}_7\text{H}_{13}$  radicals. The hydride ion transfer reaction



is probably endothermic and therefore unlikely to occur. The corresponding reactions between  $\text{c-C}_6\text{H}_{10}^+$  and  $\text{c-C}_6\text{H}_{12}$  is 22 kcal/mole endothermic.

From these possible mechanisms for the inhibition of the secondary reaction (47) there is no apparent reason why the maximum MC yield should be the same in both  $\text{ND}_3$  and  $\text{C}_2\text{H}_4$ .

The increase of MC yield with temperature in pure MCH was suggested to be due to a secondary reaction destroying MC that was less efficient at higher temperatures. If reaction (47) is the secondary reaction causing this temperature effect of MC then at higher temperatures the  $\text{C}_7\text{H}_{14}^+$  must undergo an alternative reaction. This alternative reaction must not result in the formation of  $\text{C}_7\text{H}_{13}$ , otherwise the dimer yield should also increase with temperature. No temperature effect on the dimer yield was observed. Fragmentation of the ion to lower molecular products is a possible alternative reaction of  $\text{C}_7\text{H}_{14}^+$  that would be favored at higher temperature.

The increases of MC and dimer yields in the MCH- $\text{CCl}_4$  and MCH- $\text{N}_2\text{O}$  mixtures are probably due to special effects that were observed



in these systems, and will be discussed in a subsequent section.

### 5. Unknown Products (Unk. C<sub>5</sub>-C<sub>6</sub>)

The yield of these unknown products were measured in each of the additive systems except CCl<sub>4</sub>. The value of g(unk. C<sub>5</sub>-C<sub>6</sub>) was unchanged by the addition of SF<sub>6</sub>, N<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>. With DI the experimental scatter was large but there was no significant change in the yield up to 8 mole percent. The slightly higher yield at less than 1% DI may have been due to the formation of CH<sub>3</sub>I, as mentioned earlier in the methane discussion. The most significant change of unk. C<sub>5</sub>-C<sub>6</sub> yield is in the presence of ND<sub>3</sub>, where it is reduced to zero by the addition of 10 mole percent ND<sub>3</sub>. Since ND<sub>3</sub> scavenges positive ions, the decrease of the unk. C<sub>5</sub>-C<sub>6</sub> yield by ND<sub>3</sub> indicates that this product was formed from a positive ion. There was no corresponding decrease of CH<sub>4</sub> with added ND<sub>3</sub> which indicates that the unknown product is not a C<sub>6</sub> compound but probably a C<sub>5</sub>. This is consistent with its tentative identification as a C<sub>5</sub> olefin made previously in the discussion of pure MCH radiolysis.

### C. Additive Systems with Special Effects

#### 1. Methylcyclohexane-Carbon Tetrachloride

The radiolysis of MCH-CCl<sub>4</sub> mixtures results in the formation of chloroform and methycyclohexylchloride (MCCl). The large yields of these products indicate that they are formed from a chain reaction (Figures III-19 and III-20). The yields of both MC and dimer were

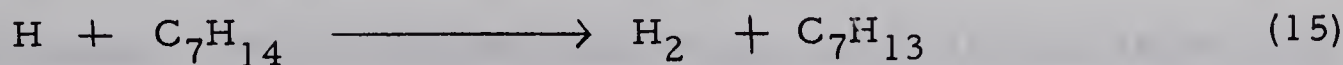
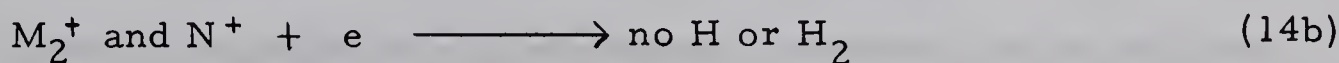
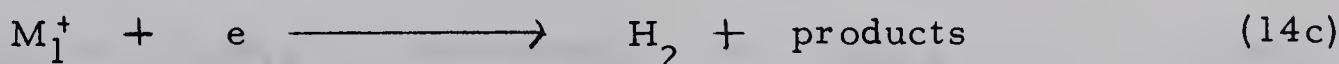
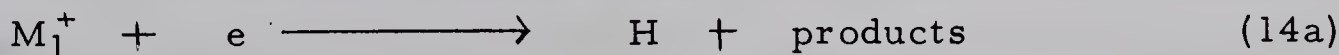
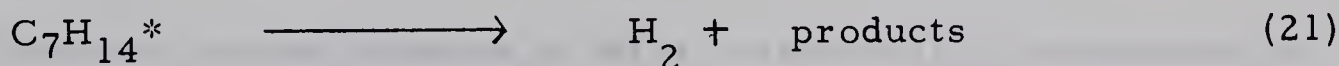
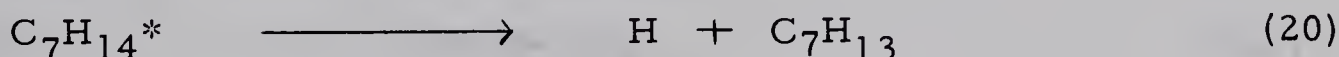
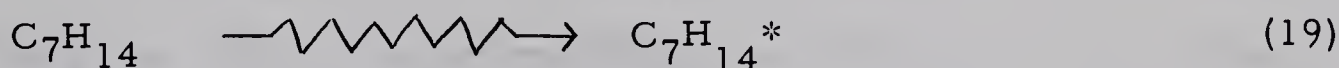
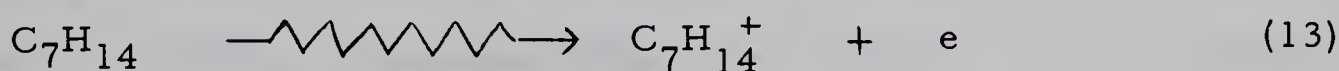




increased by the presence of  $\text{CCl}_4$  in the MCH (Figure III-21). Hexachloroethane (Figure III-19) and hydrogen chloride (Figure III-18) were also major products from the radiolysis of MCH- $\text{CCl}_4$  mixtures.

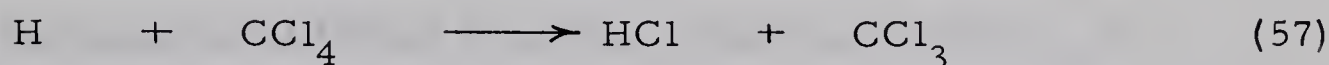
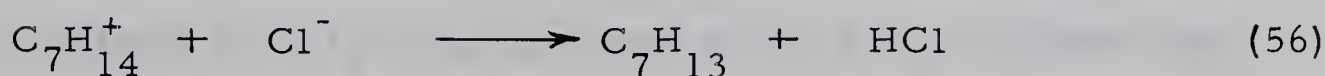
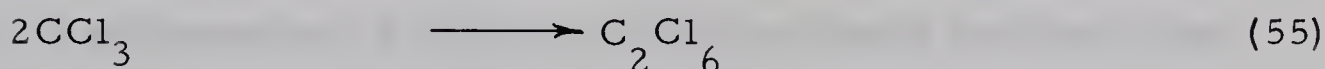
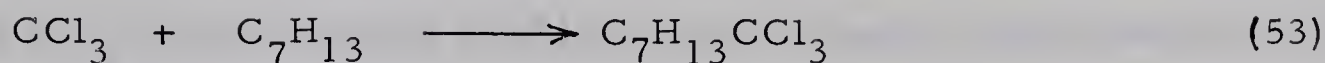
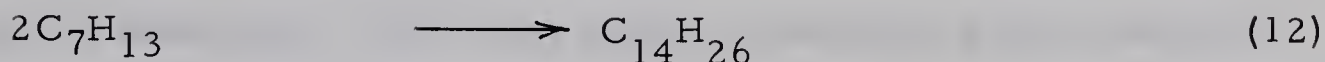
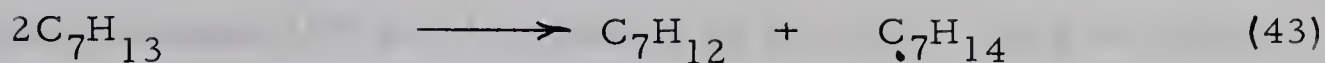
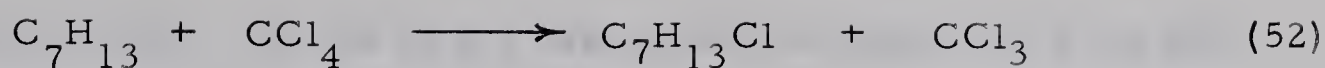
Chain reactions are commonly observed in radiolysis systems containing polyhalogen compounds such as  $\text{CCl}_4$  (123). The formation of chloroform and cyclohexyl chloride by a chain mechanism was reported by Stone and Dyne in the liquid phase radiolysis of cyclohexane-carbon tetrachloride solutions (124). The chain was propagated by  $\text{CCl}_3$  and  $\text{C}_6\text{H}_{11}$  radicals and terminated by radical-radical reactions of these radicals.

A chain mechanism involving a similar propagation and termination reactions is proposed to account for the formation of products in the vapor phase radiolysis of MCH- $\text{CCl}_4$  mixtures. The mechanism is outlined below.

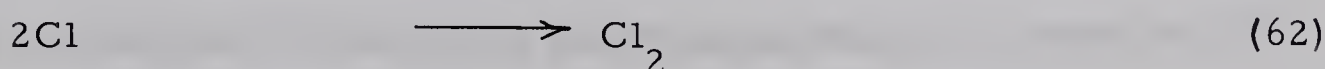
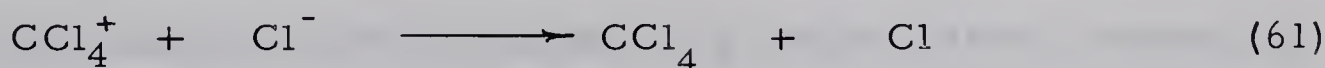
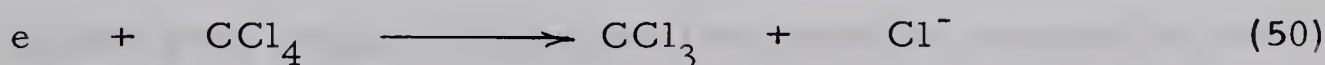
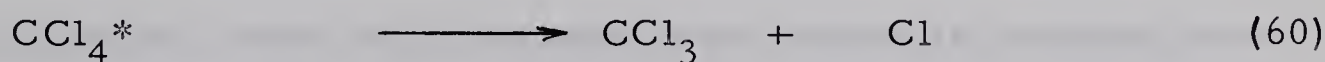
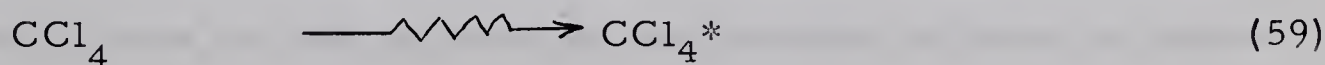
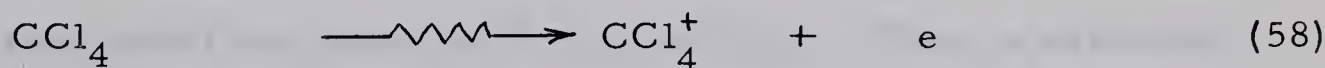




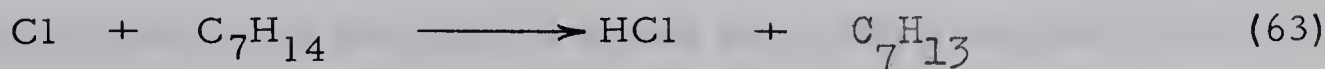




As the concentration of  $\text{CCl}_4$  increases, the contribution of direct radiolysis of  $\text{CCl}_4$  to the mechanism becomes important. The direct radiolysis of pure  $\text{CCl}_4$  is represented below.



However, in the presence of MCH, reaction (62) is replaced by reaction (63)



Carbon tetrachloride was mentioned previously as an efficient electron scavenger. The hydrogen yield (Figure III-17B) from MCH- $\text{CCl}_4$  mixtures suggested that electron scavenging was complete at less than



2 mole percent  $\text{CCl}_4$ . If this is the case then from  $G(e) = 4.4$  the HCl yield from the reactions (50) and (56) should be  $G = 4.4$ . This is approximately the yield observed. The contribution of reaction (57) to the HCl yield at low  $\text{CCl}_4$  concentrations ( $<5\%$ ) is small because in this concentration region a negligible fraction of the hydrogen yield due to H atoms is scavenged. The formation of HCl from chlorine atoms produced from the direct radiolysis of  $\text{CCl}_4$  is unimportant at low  $\text{CCl}_4$  concentration. Therefore the value of  $G(\text{HCl})$  at less than 2 mole percent  $\text{CCl}_4$  is primarily due to scavenging of electrons produced in reaction (13). Since the electron yield from direct radiolysis of  $\text{CCl}_4$  is  $G(e) = 4.1$  ( $W_{\text{CCl}_4} = 24.3$ ) (125) compared to  $G(e) = 4.4$  for MCH there should be little change of the electron yield from pure MCH to pure  $\text{CCl}_4$ . This is assuming that the two solvents act only as diluents with respect to their ion yields. Thus the yield of HCl from electrons should be essentially constant over the whole concentration range. There are two possible sources for the increase of HCl observed with increased  $\text{CCl}_4$  concentration; scavenging of H atoms by reaction (57) and from Cl atoms produced by reaction (60) abstracting H from MCH (reaction 63).

It was suggested in previous sections that in pure MCH radiolysis all of the ions produced do not yield H atoms and  $\text{C}_7\text{H}_{13}$  radicals (reactions 14a and 14b). However in the presence of a small amount of  $\text{CCl}_4$  all of the electrons are scavenged to form chloride ions which react according to reaction (56) to yield a  $\text{C}_7\text{H}_{13}$  radical. In addition, the  $\text{CCl}_3$  radical







formed on electron capture by  $\text{CCl}_4$  reacts with MCH to form another  $\text{C}_7\text{H}_{13}$  radical in reaction (51). At low  $\text{CCl}_4$  concentration there is therefore an increased concentration of  $\text{C}_7\text{H}_{13}$  radicals in the system compared to pure MCH. This results in an increase of  $G(\text{MC})$  and  $G(\text{dimer})$  as shown in Figure III-21, because of reactions (43) and (12). When the  $\text{CCl}_4$  concentration is increased reaction (52) becomes more important. This reaction serves to remove  $\text{C}_7\text{H}_{13}$  radicals and replace them with  $\text{CCl}_3$  radicals. The effect of an increased  $\text{CCl}_4$  concentration is to decrease the  $\text{C}_7\text{H}_{13}$  concentration and increase the  $\text{CCl}_3$  concentration. Reaction (57) also results in the replacement of a  $\text{C}_7\text{H}_{13}$  radical by  $\text{CCl}_3$ . The dominant chain termination step then changes from reactions (12) and (43) to reactions (53), (54), and (55). This is shown by the decrease of the MC and dimer yields and the increase of the  $\text{C}_2\text{Cl}_6$  yield as the percent  $\text{CCl}_4$  is increased. The contribution of the cross termination process, reaction (54), cannot be determined since both the products of this process are also formed from other reactions. The combination reaction between  $\text{C}_7\text{H}_{13}$  and  $\text{CCl}_3$  is shown to be small by the low yields of  $\text{C}_7\text{H}_{13}\text{CCl}_3$ .

The proposed mechanism for MCH- $\text{CCl}_4$  radiolysis suggests that there should be an equivalent number of  $\text{C}_7\text{H}_{13}$  and  $\text{CCl}_3$  radicals. The yield of each of the radicals at a particular composition can be estimated from the yields of the products formed from that radical. The yield of  $\text{C}_7\text{H}_{13}$  radicals is given by



$$G(C_7H_{13}) = 2(G(MC) + G(dimer)) + G(MCCl) + G(C_7H_{13}CCl_3)$$

and the yield of  $CCl_3$  by

$$G(CCl_3) = 2G(C_2Cl_6) + G(CHCl_3) + G(C_7H_{13}CCl_3)$$

The radical yields at different concentrations are shown in Table IV-2.

Within about 10%, Table IV-2 shows there are equivalent yields of  $C_7H_{13}$  and  $CCl_3$  radicals, as was predicted by the mechanism.

## 2. Methylcyclohexane-Nitrous Oxide

In addition to the reduction of  $g(H_2)$  mentioned previously, there is a large yield of nitrogen produced and the yields of MC and dimer are enhanced in the radiolysis of MCH- $N_2O$  mixtures. (Figures III-22, III-23). The value of  $g(N_2)$  rises to a plateau value of 16.5 at 3 mole percent  $N_2O$ . (The quantity  $g(N_2)$  is the nitrogen yield based on energy absorbed by MCH only, corrected for the nitrogen formed by the direct radiolysis of  $N_2O$ ). At the same time the MC and dimer yields reach plateaus at  $g = 16.5$  and  $1.6$  respectively. There was no significant pressure effect on these product yields in the range from 50 to 500 Torr. The yield of nitrogen, MC and dimer were temperature dependent at  $N_2O$  concentrations above 0.5 mole percent (Figures III-25, III-26, III-27). At 0.01 mole percent  $N_2O$  only  $g(MC)$  was affected by increased temperatures. This increase was much the same as observed in the temperature study of pure MCH and is likely due to secondary reactions as discussed previously.

Information about the precursors to these enhanced yields was



TABLE IV-2Radical Yields from MCH-CCl<sub>4</sub> Mixtures

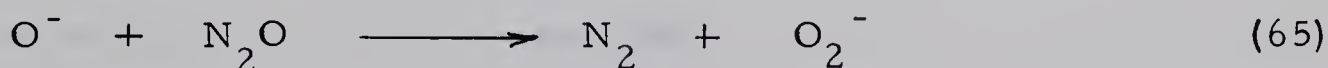
Mole % <u>CCl<sub>4</sub></u>	<u>G(C<sub>7</sub>H<sub>13</sub>)</u>	<u>G(CCl<sub>3</sub>)</u>
0.112	9.3	6.8
0.762	27.9	23.7
4.11	38.6	38.4
7.82	40.5	40.1
12.0	49.8	46.3
16.4	50.4	46.7
28.8	46.9	42.2
43.7	44.0	46.0
63.2	35.0	37.9





obtained from the addition of  $\text{SF}_6$  or DI to the  $\text{MCH-N}_2\text{O}$  mixtures. Both  $\text{SF}_6$  and DI can compete with  $\text{N}_2\text{O}$  for electrons, therefore the observed reduction of the nitrogen, MC and dimer yield by  $\text{SF}_6$  or DI in  $\text{MCH-N}_2\text{O}$  mixtures, suggests that these products were formed from electron precursors (Figures III-37 to III-40). Nitrogen was reduced to  $g < 0.5$  and MC and dimer reduced to the values observed when DI or  $\text{SF}_6$  were present alone in MCH. Similarly, Johnson and Warman (76) found that  $\text{SF}_6$  or  $\text{CCl}_4$  prevented nitrogen formation in the radiolysis of propane- $\text{N}_2\text{O}$  mixtures.

The reactions,



proposed by Johnson and Warman are not adequate to explain the large yields of nitrogen observed from  $\text{MCH-N}_2\text{O}$  mixtures. The maximum  $g(\text{N}_2)$  that can be obtained by reaction (64) and (65) in  $\text{MCH-N}_2\text{O}$  is twice the electron yield, i.e.  $g(\text{N}_2) = 8.8$ , compared with  $g(\text{N}_2) = 22.3$  observed.

To explain the observed results a mechanism must meet the following requirements:

- nitrogen, MC and dimer yields rise with increasing  $\text{N}_2\text{O}$  concentration to plateau values that are independent of further increases of  $\text{N}_2\text{O}$  concentration,
- $\text{H}_2\text{O}$  is a radiolysis product,
- the enhanced yields of nitrogen, MC and dimer are reduced by



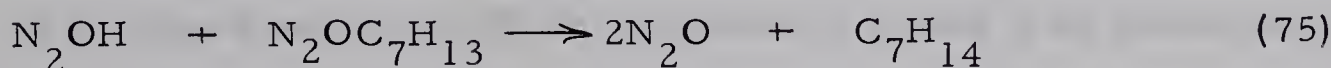
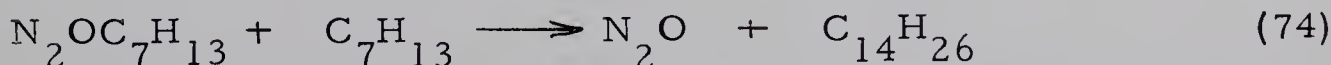
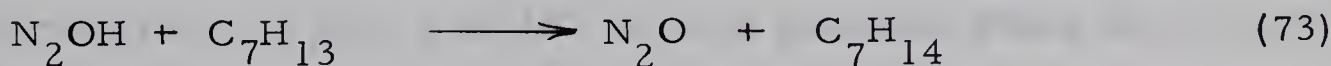
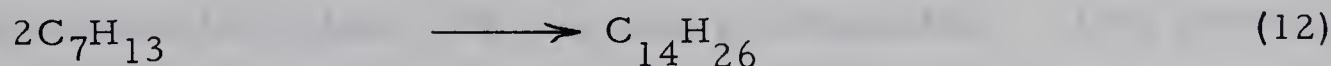
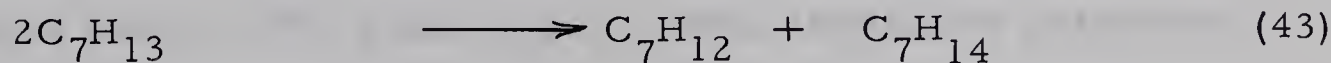
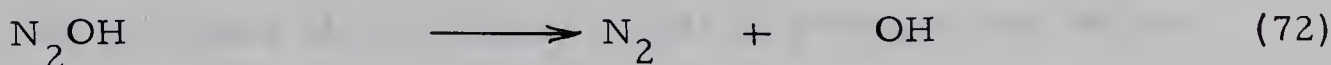
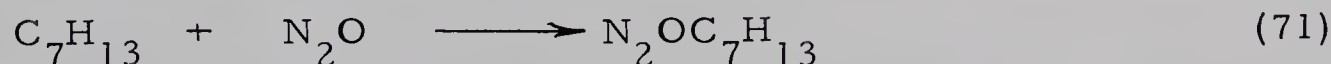
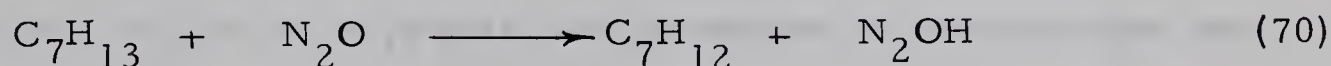
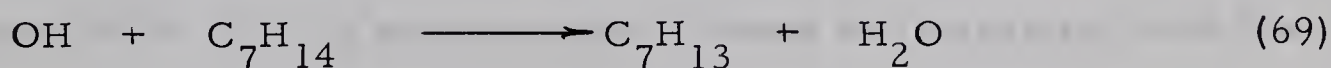
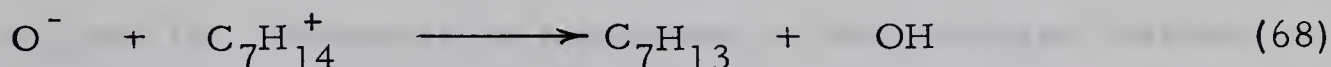
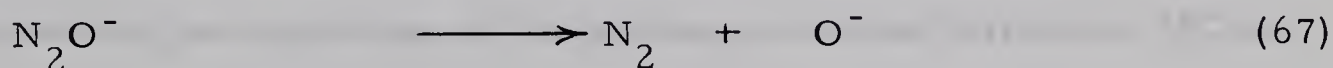
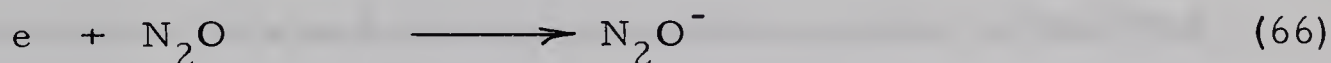
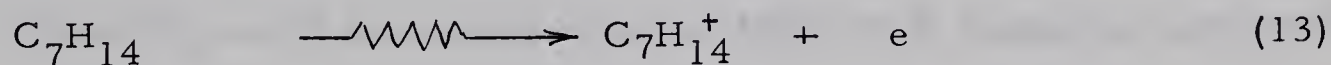
addition of  $\text{SF}_6$  or DI,

- the total hydrogen yield does not increase to  $g = 6.4$  when the nitrogen yield is suppressed by DI, (mentioned in the hydrogen discussion section B-1.)

- the plateau yield of nitrogen, MC and dimer decrease at high temperatures,

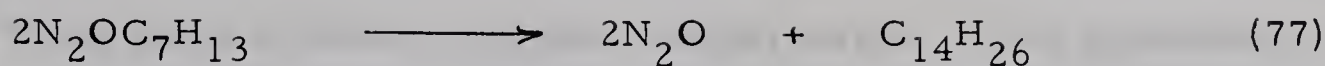
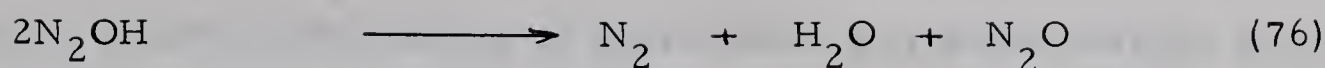
- there are temperature plateaus in nitrogen and MC yields at low  $\text{N}_2\text{O}$  concentrations.

The following reactions can be used as a starting point, but are inadequate for a complete mechanism.









The above chain mechanism, with termination by radical-radical reactions involving  $\text{C}_7\text{H}_{13}$ ,  $\text{N}_2\text{OH}$ , and  $\text{N}_2\text{OC}_7\text{H}_{13}$  can account for the increase of nitrogen, MC and dimer with increasing  $\text{N}_2\text{O}$  concentration, and for the formation of water as a radiolysis product. As the  $\text{N}_2\text{O}$  concentration is increased reactions (70) and (71) become the only fate of the  $\text{C}_7\text{H}_{13}$  radical. Under these conditions chain termination involves only  $\text{N}_2\text{OH}$  and  $\text{N}_2\text{OC}_7\text{H}_{13}$  and the yields of nitrogen, MC and dimer are independent of  $\text{N}_2\text{O}$  concentration.

When  $\text{SF}_6$  or DI are present in the  $\text{MCH-N}_2\text{O}$  mixtures competition for the electrons occurs and the chain initiation process is inhibited. This accounts for the reduction of the plateau yields of nitrogen, MC and dimer by  $\text{SF}_6$  and DI. However as mentioned in the hydrogen discussion, in the case of  $\text{MCH-N}_2\text{O-DI}$  mixtures the DI must be interacting with the  $\text{N}_2\text{O}^-$  in such a way so as to prevent the formation of both nitrogen and hydrogen.

The decrease of the plateau yields of nitrogen and MC at temperatures above  $110^\circ\text{C}$  would require some alternative reaction of  $\text{C}_7\text{H}_{13}$  that became important with increasing temperature. One possibility may be the reaction of  $\text{C}_7\text{H}_{13}$  with MC to form products which do not carry the chain.

At 0.5 mole percent  $\text{N}_2\text{O}$  the increase of yields with temperature



may be due to reaction (72) having an appreciable activation energy, and therefore being more efficient at higher temperatures. The appearance of a temperature plateau may then be due to removal of  $C_7H_{13}$  radicals by reactions (71) plus (77). The increase in all yields above  $200^{\circ}C$  is probably due to radiation induced pyrolysis as found in pure MCH at high temperatures.

The interpretation of the results from the MCH- $N_2O$  mixtures is highly speculative. However it is clear that  $N_2O$  does not act as a simple electron scavenger in vapor phase alkane radiolysis. This can be further shown by the difference of nitrogen yields from the vapor phase radiolysis of cyclopentane or MCH- $N_2O$  mixtures. In cyclopentane- $N_2O$  mixtures  $g(N_2) \approx 12$  (measured in this laboratory) and in MCH- $N_2O$   $g(N_2) = 22$ , while the electron yields calculated from W-values, for each of these compounds are in the range from  $g(e) = 4.0$  to  $4.5$ .





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## APPENDIX

Calculation of Stopping Power Ratios

The rate of energy loss for fast electrons is given by Bethe's

equation (23)  $-\frac{dT}{dx}_{\text{coll}} =$

$$\frac{2\pi e^4 Z N}{m_0 v^2} \left[ \ln \frac{m_0 v^2 T}{2I^2(1-\beta^2)} - (2\sqrt{1-\beta^2} - 1 + \beta^2) \ln 2 + (1-\beta^2) + \frac{1}{8}(1-\sqrt{1-\beta^2})^2 \right] \quad (1)$$

where  $\frac{dT}{dx}$  = collisional energy loss per cm. of path length, ergs/cm =  
stopping power

$N$  = molecules/cc = (molecules/mole) x (moles/cc)

$$6.02 \times 10^{23} \times \text{moles} / \text{Volume (V)}.$$

$Z$  = electrons/ molecule

$e$  = electronic charge =  $4.80 \times 10^{-10}$  esu

$T$  = relativistic kinetic energy of electron, assumed to be

0.6 Mev ( $9.6 \times 10^{-7}$  ergs) for  $^{60}\text{Co}$   $\gamma$ -radiation

$v$  = velocity of electron =  $c \sqrt{1 - (1 + \frac{T}{m_0 c^2})^{-2}} = 2.7 \times 10^{10}$  cm/sec

$c$  = velocity of light =  $3.0 \times 10^{10}$  cm/sec

$m_0$  = rest mass of electron =  $9.11 \times 10^{-28}$  g

$\beta$  =  $v/c$  = 0.89

$I$  = average excitation potential for molecule

$$\ln I = \frac{N_1 Z_1 \ln I_1 + N_2 Z_2 \ln I_2 + \dots}{N_1 Z_1 + N_2 Z_2 + \dots}$$





where  $N_1$  = number of atoms of element 1 per molecule

where  $Z_1$  = number of electrons per atom of element 1

where  $I_1$  = average excitation potential of element 1

If the number of cc(V) is kept constant and the calculation is done for 1 mole of gas then

$$N = \frac{6.02 \times 10^{23}}{V}$$

Define  $\frac{dT}{dx}'$  = rate of energy loss per cm per mole, ergs/cm/mole

$$\text{then } \frac{dT}{dx}' = K Z \left[ \ln \frac{A}{I^2} + B \right] \quad (2)$$

$$\text{where } K = \frac{2 \pi e^4 (6.02 \times 10^{23})}{m_o v^2 V}$$

$$A = \frac{m_o v^2 T}{2(1 - \beta^2)} = 1.5 \times 10^{-12}$$

$$B = -(2 \sqrt{1 - \beta^2} - 1 + \beta^2) \ln 2 + (1 - \beta^2) + \frac{1}{8} (1 - \sqrt{1 - \beta^2})^2 = -0.24$$

The relative stopping power per mole for compounds 1 and 2 is given by

$$\rho^1_2 = \frac{(dT/dx)'_1}{(dT/dx)'_2} = \frac{Z_1}{Z_2} \left[ \frac{\ln A/I_1^2 + B}{\ln A/I_2^2 + B} \right]$$

The values of  $Z$ ,  $I$ , and  $(dT/dx)'$  for the various material used in this project are given in the following table.



Material	Z	I		$(dT/dx)^1$
		(ev)	(ergs)	
MCH	56	52.5	$8.44 \times 10^{-11}$	$K(1.06 \times 10^3)$
$C_2H_4$	16	50.5	$8.09 \times 10^{-11}$	$K(3.04 \times 10^2)$
$CCl_4$	74	160	$2.57 \times 10^{-10}$	$K(1.23 \times 10^3)$
$N_2O$	22	91.6	$1.47 \times 10^{-10}$	$K(3.91 \times 10^2)$
$SF_6$	70	117	$1.88 \times 10^{-10}$	$K(1.21 \times 10^3)$
HI	54	515	$8.24 \times 10^{-10}$	$K(7.74 \times 10^2)$
$NH_3$	10	54.2	$8.70 \times 10^{-11}$	$K(1.88 \times 10^2)$
Air	14.4	85	$1.4 \times 10^{-10}$	$K(2.58 \times 10^2)$







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